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# FIRE AND EXPLOSION RISKS.

A HANDBOOK DEALING WITH THE DETECTION, INVESTIGATION  
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AND EXPLOSIONS OF CHEMICO-TECHNICAL  
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FOR THE USE OF FIRE INSURANCE OFFICIALS, FIRE BRIGADE  
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AND FACTORY OWNERS.

BY

DR. VON SCHWARTZ.

TRANSLATED FROM THE REVISED GERMAN EDITION BY  
CHARLES T. C. SALTER.



LONDON:  
CHARLES GRIFFIN AND COMPANY, LIMITED;  
EXETER STREET, STRAND.

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## PREFACE

OF late years great strides have been made in chemistry in connection with Fire Assurance, the prevention and extinction of fires, and the detection of the causes of accidental or premeditated outbreaks; in fact, chemistry has become an indispensable aid in the solution of these important problems.

Keeping pace with the development of our civilisation, we may expect that, in the future, the assistance of chemistry will be more and more relied on in the regulation of insurances, the promulgation of legal enactments against fire risk, the detection of incendiarism, and in cases of dispute before the courts. In such eventualities two ways are open, viz. :—

1. *Calling in the aid of a chemist*, a proceeding not always feasible, oftentimes expensive, and sometimes unsatisfactory, owing to the available chemist being imperfectly versed in the matter of fire prevention.

2. *Consulting the literature*. This resource also is not always available to the officials interested; and even when it is, the information respecting fire prevention is scattered over such a wide area, as to necessitate special study in order to separate the desired particulars from the enormous bulk of the literature itself. In fact, apart from a few special treatises, such as Professor Häpke's interesting work on "Spontaneous Ignition," Dr. M. Richter's book on "Benzine Fires," and Meunier's old work, there is at the present time no single book dealing so fully with fire risks and fire prevention, in the domain of chemical technology, as to be suitable for all cases, and for the laity.

Perhaps, also, no such work will ever be written, since any attempt to accomplish this task would have to deal with the most divergent local conditions and materials, the most complicated

processes, the incalculable peculiarities of the materials: in short, to struggle unsuccessfully with unconquerable difficulties. The well-defined individuality of each separate article of insurance: the works and plant, the raw material, the intermediate products, waste products and finished article, to say nothing of the individuality of each case of fire, often due to a problematical cause and complicated inception, even under comparable circumstances—all these factors prevent generalisation, and militate against the compilation of a work that shall be applicable to all conditions. They also explain why the activity of the chemist in this connection—like that of the jurist in his branch—must be continuous and unremitting.

If, in despite of all this, I have undertaken the compilation of a work directed to the solution of some of these important problems, the step in question is taken solely with the idea of facilitating the utilisation of the chemico-technical literature by officials of Fire Insurance Companies, Fire Brigades, the Judiciary, Law Officers of the State, the Police, &c., who have not had a chemical training, and to place in the hands of these officials a popular guide, which will give them information—so far as the chemical aspect of the matter is concerned—on the degree of fire risk, the possibility and means of prevention, incendiarism, and the causes of fires, as well as extend their general knowledge of the fire risk of chemico-technical substances and processes, without requiring any previous acquaintance with the subject.

In all the contingencies here in question, a general acquaintance—up to a certain extent—with the risk of fire and explosions may be of great importance; but the attainment of this necessary knowledge is a difficult matter for those who have not had a chemical training; and however interesting chemistry may be to all classes of mankind, the professional investigation of chemical problems is often very difficult to non-chemists.

Many complaints in this respect have reached the author in the course of a career extending over a quarter of a century as works chemist, commercial chemist, and finally as factory inspector for the Grand Duchies of Coburg and Gotha, and for this reason

he has decided to comply with the demand by issuing a practical handbook, to serve as a work of reference and a means of study.

The work is not designed to form an introduction to the variable practices of Fire Insurance Companies, or a mere repetition of Trade Union regulations for the prevention of accidents; neither is it the author's intention to deal with all the separate branches of technology, since such a course would lead him too far away from the object in view, namely: To present non-chemists with a practical chemical tool, and to facilitate investigation of the, to them, foreign domain of chemical technology in questions of fire risk and fire prevention.

With this idea in view I have decided to make use, in many instances, of older chemical conceptions, because I regard the same as more suitable to, and readily understandable by, non-chemists, and am of opinion that, for detecting, judging, and correctly settling cases of fire or combustion, it is more important that the non-chemist should treat and decide the matter in accordance with a standpoint he understands, rather than proceed according to new theories which he is incapable of assimilating, and which are, moreover, still subjects of scientific controversy.

In answer to the objection that the book overestimates—to the advantage of Fire Insurance Companies—certain dangers of individual trades and substances (an objection that was also urged against Meunier's work in its day), I would urge that a work of this kind ought to bear in mind the *possibilities* of danger. Be these latter never so remote, they must not be left out of consideration if individual instances have demonstrated them to be within the bounds of possibility. The fire risk of a substance or process is not to be judged of by the extent or the number of fires to which it has given rise: nevertheless, it should be known to the officials connected with Fire Insurance Companies, the Judiciary, or the Fire Brigade, that, under certain conditions, an otherwise harmless material may become a very dangerous one, nor should one wait for the destruction of large factories, or the occurrence of numerous explosions, to prove its highly dangerous character. The author considers that with the reports of these possibilities of danger

before them those officials should proceed in a rational manner, and not always class such instances on a par with direct dangers.

In all places where risk or danger is mentioned in the text, it will be understood to refer solely to fire, spontaneous ignition, or explosion, hygienic dangers being left out of consideration.

I have avoided the description of typical cases of fire and explosion, it being always objectionable, in this domain particularly, to correlate occurrences that are mostly based on entirely different conditions.

Temperatures are given throughout in degrees of the Centigrade thermometer, except where specially stated otherwise.

May the work fulfil its purpose, as a reliable *vade mecum* and adviser for the non-chemist in the, to him, unfamiliar subject of Chemistry.

DR. VON SCHWARTZ.

CONSTANCE, September, 1901.

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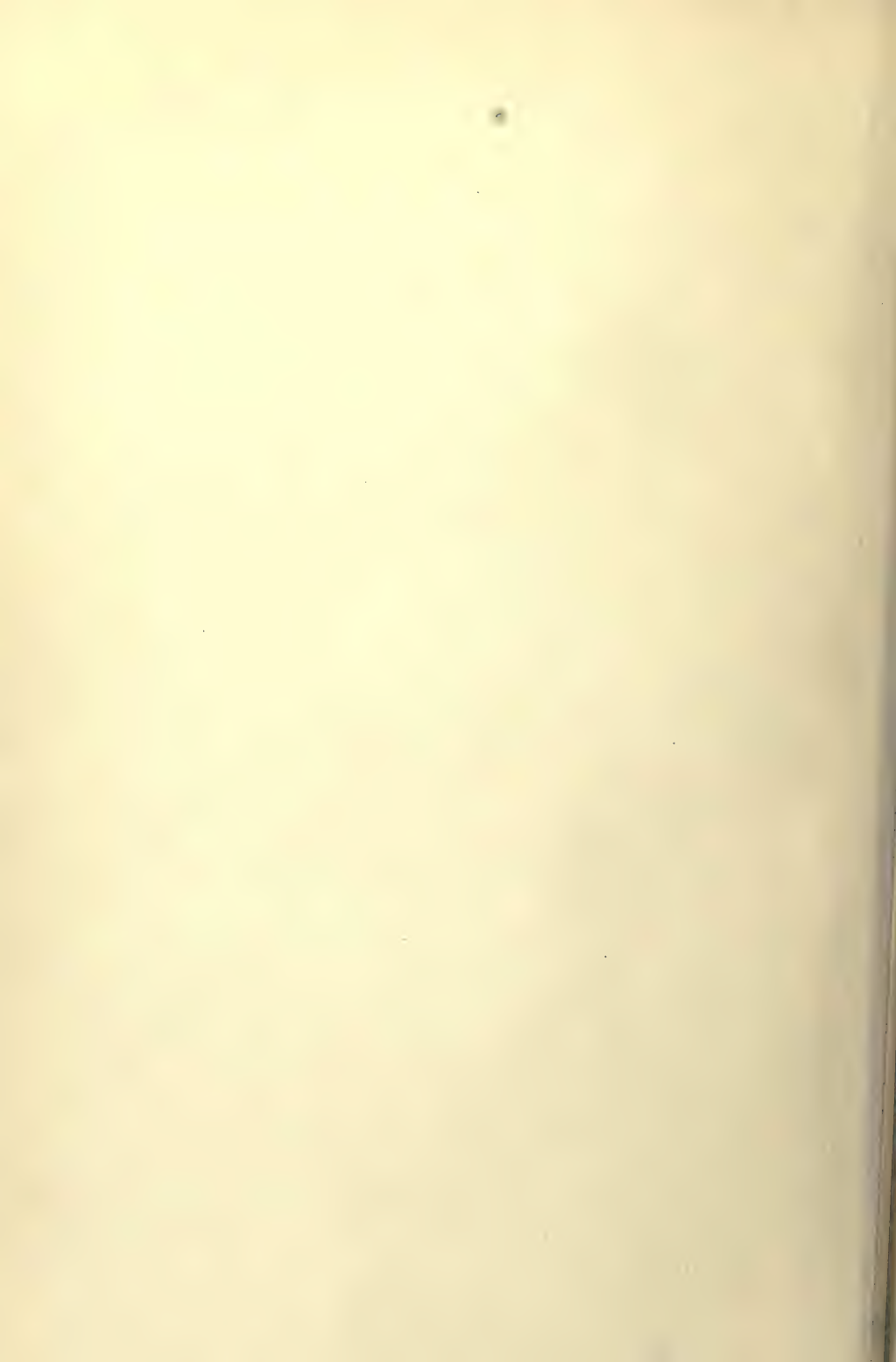
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# PART I—GENERAL

## CHAPTER I

### TEMPERATURE

ALTHOUGH at the present time particular endeavours are being made, in connection with Chemical and Mechanical Technology, to simplify methods for obtaining the highest possible temperatures, and utilise their effects to the best advantage, equal attention is being devoted to low temperatures as well.

For insurance purposes low temperatures are of importance, inasmuch as they afford the best of all protections against the inception and development of fire. Substances cooled down to  $-80^{\circ}$  C. will no longer burn, and cannot be ignited at all, since at this temperature chemical reactions proceed only with great difficulty, and at  $-125^{\circ}$  C. are rendered almost impossible. Consequently, the occurrence of fires could be precluded by cooling articles down to this temperature. On the other hand, these low temperatures—the lowest hitherto attained is  $-257^{\circ}$  C.—are attended with great objections, particularly for insurance companies, since it is only by the application of gases, employed under high pressures (up to 250 atmospheres), that they can be attained at all; and this method leads to danger of explosion, the explosion risk of gases being increased by pressure.

When only such gases as ammonia, nitrogen, sulphur dioxide, or carbon dioxide are in question, the danger is purely one of explosion, that is to say, there is no risk of fire, unless the explosion should act upon explosive or readily inflammable bodies, gas pipes, or installations for heating or lighting, and thereby give rise to damage.

In the case of nitrous oxide or oxygen, however, direct danger of fire from the explosion of the gases is imminent, even if not of invariable occurrence. On the other hand, when readily inflammable, combustible gases, such as sulphuretted hydrogen, coal gas, acetylene, hydrogen gas, or marsh gas, are compressed to the liquid condition, explosions of same are accompanied by flame, and in most instances will be followed by fire, unless the explosion occurs in a fireproof place.

Low temperatures are often employed for purposes of purification, or for the production of absolutely chemically pure preparations. Ether, alcohol, methyl chloride, ethyl chloride, and certain alcoholic preparations are obtained in the desired state of purity by the aid of compressed gases, the evaporation of which produces cold; but although these substances are more or less explosive, yet, under the conditions specified,

their powers of chemical reaction are greatly enfeebled, and consequently the risk is on a lower plane than usual.

Substances of high chemical energy, which enter into combination in an explosive manner at ordinary temperatures, *e.g.* potassium and sulphuric acid, can be mixed together mechanically at  $-70^{\circ}\text{C}$ . without uniting. The reason for the prolonged delay in the first successful preparation of liquefied gases was due to the erroneous assumption that only pressure or cold alone was necessary; but the conviction has now arisen that the conjoint action of high pressure and extreme cold is essential to effect the liquefaction of the so-called permanent gases and air; consequently, the greater the degree of cooling, the weaker may be the pressure. The temperature to which a gas *must* be cooled before it can become liquid at the lowest pressure differs with each gas, but has been accurately determined; and above this temperature the gas cannot be liquefied, however great the pressure employed. This temperature is known as the "critical temperature" of the gas, and the lowest pressure at which a gas can be liquefied, after being cooled to the critical temperature, is termed "critical pressure."

The following table gives the critical temperatures and pressures of the most important gases:

	Critical Temperature.	Critical Pressure.	Boiling Point of the Liquid.
	Degrees C.	Atmospheres.	Degrees C.
Sulphur dioxide (sulphurous acid).	+155	79	-8
Carbon dioxide (carbonic acid) .	+31	74	-80
Ethylene . . . . .	+13	52	-102
Sulphuretted hydrogen . . . .	+10	15	-74
Nitric oxide . . . . .	-93	71	-154
Methane (marsh gas) . . . . .	-82	55	-164
Oxygen . . . . .	-119	50	-182
Argon . . . . .	-121	50.6	-185
Carbon monoxide (carbonic oxide)	-140	35	-190
Air . . . . .	-140	39	-191
Nitrogen . . . . .	-146	35	-194
Hydrogen . . . . .	-234	20	-243
Ammonia . . . . .	+130	115	-34

Progress similar to that made in the attainment of low temperatures has to be recorded at the opposite end of the scale, partly owing to the introduction of the electric furnace, partly to the Goldschmidt Aluminium (Thermit) process, and also to methods of burning one or more gases in special forms of apparatus.

By means of the electric furnace it is found possible to melt and volatilise bodies (metals) hitherto regarded as refractory and non-volatile; temperatures of  $3000^{\circ}\text{C}$ . can be attained with ease, and even as high as  $3500^{\circ}\text{C}$ . under certain circumstances; lime, chromium oxide, and magnesia can be fused (at  $2250^{\circ}$ – $2500^{\circ}\text{C}$ .), and gold, platinum, manganese, silicon, and even carbon can be volatilised. The electric furnace is employed for the preparation of these substances, or certain of their compounds, *e.g.* calcium carbide, in which event great care must be bestowed on the insulation of the conducting wires.

By reason of its simplicity, the Goldschmidt process is adapted to

replace flame or glowing heat as a means of producing high temperatures in many cases, *e.g.* the production of artificial diamonds. No flame ever gives off the actual heat generated in its combustion, the reason being that a portion of this heat is consumed by the flame for its own purposes, and at no point in the flame does the combustion pursue a normal course. On this account ingenious appliances have been devised for conducting two different gases into a burner common to both, and concentrating the flame to the smallest possible bulk, whereby far higher temperatures than usual can be produced ( $2840^{\circ}$  C. in the oxyhydrogen blowpipe). Apart, however, from its expensive character, the unsuitability of the gas blowpipe for certain purposes militates against its general employment, and it is here that the Goldschmidt process finds its uses.

Powdered metallic aluminium is inflammable and burns to alumina, with disengagement of great heat, risk of explosion being not altogether precluded. This danger, however, is obviated by Goldschmidt, in that, instead of igniting the whole of the aluminium at once, he effects the ignition at one point therein, from which point it then gradually extends throughout the entire mass.

This initial difficulty of igniting at a single point, in order to prevent the whole mass becoming heated and burning in an explosive manner, is overcome by using an igniting pellet, composed of barium peroxide or other carrier of oxygen (*q.v.*); the pellet itself is lighted by means of a magnesium wire, which burns on applying a match, whereupon the carrier of oxygen liberates that gas, in presence of which the metallic aluminium burns with great readiness, accompanied by the production of a high temperature. The mixture of aluminium and ferric oxide is called thermite.

The article to be treated, soldered, fused, or reduced is embedded in the mass of internally, though slowly, glowing aluminium, where it is exposed to a temperature of about  $2500^{\circ}$ – $3000^{\circ}$  C.

The value of the process lies in the fact that the heat is liberated within a very small space and relatively short time.

The loss of heat by external radiation is so slight that the process may be performed in a cigar box, without injury to the latter; consequently, if carried out strictly in accordance with the instructions, the process is free from danger of fire or explosion. Of course, great care should be exercised in the handling and storage of the igniting pellets, even when only a few are kept, and the storage place must always be fireproof. In connection with the dangers accruing from metallic aluminium, see *Bronze Powders and Aluminium*.

Other means for the production of high temperatures include acetylene, and air enriched with oxygen by a process of fractional distillation of liquefied air. This Linde's air (so-called after its first producer) contains 50 per cent. of oxygen, against the 21 per cent. present in ordinary air, and therefore acts as an oxygen carrier in cases of combustion and incandescence; it generates great heat, but is unfortunately too expensive for manufacturing uses, for which purpose the price should be not more than a farthing per cubic yard.

Acetylene, being only suitable for use under considerable pressure, is not well adapted for general employment in the production of high temperatures, owing to the great explosion risk (see *Acetylene*).

High temperatures may also be produced by means of pressure. Thus, if air be compressed to 60 atmospheres, a temperature of 670° C. is obtained; at 100 atmos., 820° C.; at 200 atmos., 1060° C. These temperatures, which may best be expressed by the term "heat of compression," are quite sufficient to ignite inflammable materials like wood, paper, &c. They are chiefly utilised in blasting, where the explosives (*q.v.*) in closed bore-holes generate pressures up to 6000–8000 atmos.

The following examples of high temperatures may be given:—

- (1) Produced by detonation or combustion of gaseous mixtures in closed vessels—  
 3033° C. by carbon monoxide gas and oxygen (carbonic oxide detonating gas).  
 2844° C. by hydrogen gas and oxygen (oxyhydrogen gas).  
 1997° C. by carbon monoxide gas and air.  
 2024° C. by hydrogen gas and air.
- (2) 2844° C. in blowpipe and soldering lamps.
- (3) 3500° C. in the electric furnace.
- (4) 3000° C. in the Goldschmidt process.
- (5) 3200° C. in explosions of blasting materials.

The science of the production of high and low temperatures is still far from being complete; but, even though not yet perfect in all respects, it may be expected to cause great revolutions in various branches of technology ere long—in the manufacture of steel and glass, and in metallurgy; on which account it is desirable that fire insurance officials should give the matter a share of their attention.

In absorbing heat many substances are converted from the solid or semi-solid to the liquid state; heat diminishes the cohesion of the individual particles. The temperature at which this transition is effected is termed the "melting point" or "fusing point" (see *Table of Melting Points*, Appendix D). The same term is sometimes applied to the temperature at which the molten or fused substance is reconverted into the solid or pasty condition, because this point is more easily and accurately determined. It is, however, advisable to retain the first-mentioned conception, and denote the second phenomenon by "solidification point." In no case is there any wide divergence between the two temperatures.

In many industrial substances the melting point is of great importance as regards the fire risk, since the commencement of melting is accompanied by—

- (1) Accumulation of heat in the melting substance.
- (2) The substance is brought nearer to its flashing and ignition points.
- (3) Its affinity for oxygen (*i.e.* combustibility) is increased.
- (4) Heat may generate inflammable, explosive vapours in melted bodies, *e.g.* fats, oils, resins, lacquers, and varnishes.
- (5) Molten substances froth up readily when further heated, and then easily take fire.
- (6) Molten substances of a metallic nature readily form with water an explosive gas (oxyhydrogen gas), and thus give rise to risk of explosion.

The molten state considerably heightens the fire risk, and may even, in certain materials, produce explosibility.

The melting point of a substance remains unaltered, whatever the pressure, whereas the boiling point varies; on the other hand, the less important solidification point is raised several degrees by increased pressure.

If a liquid, or a substance that has been liquefied by heat, be further raised to such a high temperature that the vapours generated within the liquid acquire sufficient tension to overcome the weight of the column of liquid, *plus* the pressure of the superincumbent atmosphere, then the vapours will ascend in the form of bubbles and escape from the liquid, which is then considered to have attained its "boiling point" (see also *Tables of Boiling Points*, VI. and VII. in the Appendix).

The boiling point varies in accordance with the altitude, as also in consequence of artificial devices, modifications in the form and character of the vessel, and the presence of fibrous, pulverulent, and gaseous substances. Increased height above sea-level, the cooling of the stratum of air above the surface of the liquid, artificial reduction of the pressure, roughened internal surface of the vessel, and the presence of filaments, powder, or dust, all lower the boiling point. A contrary effect is produced by diminishing the altitude, artificially increasing the pressure, using a vessel with smooth inner walls, keeping the liquid clear, pure, and free from dust, and adding substances that are soluble in the liquid, or mixing with it liquids of higher boiling point.

The alterations thus effected in the boiling point are none of them so considerable as to augment or diminish the fire risk of a liquid. On the other hand, certain of these causes may greatly increase the fire risk of a liquid by the manner in which they facilitate its ebullition. Thus, for example, the addition of finely powdered substances to, or the immersion of a thread in, a liquid that is already nearly or quite boiling, may produce sudden violent ebullition, accompanied by frothing and boiling over. Should this occur with varnishes, lacquers, resins, mineral oils, tar, dissolved fats, or fatty oils, the danger of ignition will be considerable (see *Retarded Ebullition*).

Just as fusion acts in the case of solid substances, so the boiling of liquids increases their fire risk, the degree of danger becoming greater in proportion as the boiling point is lower, and therefore more speedily reached.

Substances like ether, benzine, benzol, and carbon disulphide, that boil and liberate vapour under a very small accumulation of heat, are, as a rule, very inflammable, and exhibit in a high degree the faculty of forming explosive vapour mixtures. On the other hand, the converse is not always true of high boiling points, since benzol, which boils at  $80.4^{\circ}\text{C}$ ., and therefore would seem to be less dangerous than ether and carbon disulphide (boiling at  $35.5^{\circ}$  and  $46^{\circ}\text{C}$ . respectively), must be classed as fully on a par with these substances so far as general risk of fire and explosion is concerned, since it has the same flashing and burning points as these latter, both of which factors have a determinating influence. In fact, a higher boiling point only implies diminished risk of fire and explosion when accompanied by high flashing and burning points (see this point, under *Combustion*).

Liquids that are raised to boiling point, or nearly so, by ordinary room temperature, stove heat, or the heat of the sun, under ordinary pressure and without the assistance of artificial means, may be classed as

of low boiling point, the maximum limit for this class being  $50^{\circ}\text{C}$ . (see Table V., Appendix). Medium boiling points range between  $50^{\circ}$  and  $150^{\circ}\text{C}$ ., and all above this latter temperature may be classed as high boiling points.

Under certain circumstances it is possible to heat a liquid (*e.g.* water) far above its true boiling point without the phenomena of ebullition, the ascent of bubbles, being apparent. This often paradoxical superheating chiefly occurs in liquids that are entirely free from air or gas, and are at the same time in a quiescent condition.

If a slight current of air be passed through such a liquid, or if a few grains of sand be added, or if it is slightly disturbed, ebullition will suddenly set in, sometimes with such violence that the vessel is no longer able to contain the foaming mass, or cannot withstand the pressure of the suddenly liberated vapours, the consequence being a dangerous boiling over, or, in the case of closed vessels, an explosion.

This phenomenon of delayed boiling, termed **retarded ebullition**, occurs in many liquids, but can always be prevented by a timely stirring, the addition of powdered substances, introduction of fibres, roughening the smooth walls of the vessel, injecting air, or adding aerated liquids. These precautions, however, must be taken in good time, before the boiling point is approached.

## CHAPTER II

### COMBUSTION

ALTHOUGH, from the chemical point of view, combustion proceeds in a uniform manner in all cases of fire, the causes of the same may differ considerably. For instance, combustion or fire may result from the following causes:—

- (1) Direct ignition with flaming or glowing material.
- (2) Faint, but prolonged heat.
- (3) Spontaneous heating.
- (4) Spontaneous ignition.
- (5) Explosion.
- (6) Electric sparks, flashes of lightning.
- (7) Chemical reactions.
- (8) Pressure, friction, shock, falls, concussion.
- (9) Focussed rays.

These various causes only lead to combustion and fires provided the necessary conditions for the maintenance of these phenomena be present, namely, warmth and air, or oxygen.

If the supply of oxygen (*q.v.*) be cut off from a burning substance, combustion ceases, the same result ensuing when the substance is cooled down, even though atmospheric oxygen is present (see *Temperature*).

What is understood chemically by combustion is the process whereby substances, or individual constituents of same, combine with oxygen (become oxidised) with liberation of heat.

Three factors are necessary to the course of this process: the substance to be consumed, the body (oxygen) supporting combustion, and the

disseminating factor (heat). Now, the process is far from being of such a simple character as is generally supposed, especially in cases of fire.

In the first place, the article must be raised to a certain temperature before it can burn; this temperature must be sufficient to effect direct ignition, or else to generate vapour within the substances. If, when this temperature is attained, the substance furnishes inflammable vapours as the result, the **flashing point** of the substance has been reached (see *Flashing Point*, and Table VIII., Appendix).

Even then the substance has not reached the stage of combustion, for though the inflammable vapour may have taken fire, the substance itself does not yet burn. An example of this is afforded by petroleum, which, on being heated to 23° C. or over, gives off inflammable vapours which flash on the application of a lighted match; whereas the match will be extinguished on immersion in the oil, without setting fire to the latter, because the oil has not yet reached the temperature at which it is capable of igniting and burning (the **burning point**). The flashing point, which chiefly applies to liquids—though it would be perfectly justifiable to also speak of it in connection with such solid substances as paper, wood, straw, &c., which likewise produce vapour in burning—is the prime factor in determining the fire risk of an insured article, since the lower the flashing point the greater the danger of ignition (see Table VIII.).

The inflammability of an article depends (1) on the gas it contains, and (2) on its capacity for liberating vapour (volatilising).

Several liquids evolve vapour even at -20° C., and these must be classed as extremely dangerous; the same remark also applies to such substances as give off inflammable vapours as low as 10° C.

A flashing point of 10-25° C. characterises a substance as universally dangerous; substances flashing between 25° and 60° C., however, are only dangerous indirectly, that is to say, they become dangerous only if the usual precautionary measures in storage, transport, handling, and treatment be neglected. Substances flashing at or above 60° C. have but a low fire risk, and this will only become manifest if they are brought into contact with burning or glowing bodies, or are exposed to prolonged warmth or the sudden influence of great heat.

The burning point of a substance is the temperature to which the same must attain before it will ignite on the application of a flame.

Now, whilst the flashing point of any one substance (liquids in particular) is fairly constant, the burning point may fluctuate considerably in practice, unless chemically pure substances are in question. It is influenced by the manner and extent of heating, the form, porosity, moisture content, quantity of the stored material, its age, and various other factors. Dryness, porosity, fineness of division, loose storage, low power of conducting heat, all tend to reduce the burning point, and therefore increase the risk of ignition; though exceptions are known wherein, for example, moisture lowers and dryness raises the burning point—phosphorus, for instance, igniting at 60° C. in damp oxygen, whereas in the dry gas it does not burn below 320° C. Sulphur also behaves in the same way.

The burning point is generally higher than the flashing point, though occasionally they coincide, as is the case with ether, carbon disulphide, benzol, wood spirit and petroleum ether.

Taken separately, neither flashing point nor burning point affords a criterion of the fire risk of a substance, the mutual relation of these two points being determinative. This relation must chiefly be borne in mind in cases where it is a matter of replacing a decidedly dangerous substance by another less risky one, in chemico-technical trades.

Substances with low flashing point and high burning point are more dangerous than those with high flashing point and low burning point.

A low flashing point indicates explosive tendencies.

A low burning point indicates a tendency to the production and extension of flame.

Although two substances have identical flashing and burning points, this by no means implies that they are equally dangerous, a higher boiling point possessed by one of them being indicative of greater safety; on the other hand, in the event of wide divergence in the relative flashing and burning points, the boiling point loses its importance.

In addition to the burning point there is another factor, namely, the **spontaneous ignition point**, a term expressing the temperature at which gases, vapours, or solid substances will take fire entirely of their own accord, without being brought into contact with burning or incandescent substances, but merely under the influence of heat alone, be the latter never so moderate. Moreover, there are numerous substances (see Appendix) which will ignite spontaneously (see *Spontaneous Ignition*) even at the ordinary temperature, or immediately on being brought into contact with air or water.

When a substance has passed from the flashing stage to that of combustion, and is there maintained, it has reached its **combustion point**, which term expresses the temperature at which the substance in question is consumed. In the sequence of the phenomena of combustion, the combustion point must be regarded as succeeding the burning point, in the same manner as the latter succeeds the flashing point.

The *quantity* of heat that is given off during combustion is termed the **heat of combustion**, and is measured by **heat units** or calories (*q.v.*).

In the case of chemically pure substances, which are therefore of definite chemical composition, the combustion point and heat of combustion always remain invariable; but with other organic substances, of variable composition, they may fluctuate considerably, and are influenced by the rapidity of combustion, air supply, wind, moisture, dryness, and especially cold. The entire process of fire extinction with water is based on the lowering of the combustion temperature by the cooling action of the water, depriving the burning articles of their heat of combustion, and reducing them from the combustion point to the burning point, thence to the flashing point, and then keeping them down below the latter.

Frequently, in large fires, the fire breaks out again, owing to the fact that the burning articles have been cooled to below their combustion temperature during the work of extinction, but still remain at a temperature higher than the burning point, which circumstance enables them to break out afresh at any moment. To ensure thorough extinction it is necessary to cool the burning objects not merely below the combustion point, but below the burning and flashing points as well.

Some substances exhibit the faculty of maintaining a state of combustion without manifesting more than slightly, if at all, the usual

phenomena of that condition. They do not burn in the true sense of the word, neither do they glow, their combustion consisting merely in a progressively advancing glimmering line or streak, which only liberates sufficient heat to make the adjacent portions burn or glow faintly, but is not enough to raise the whole body to the burning point or to incandescence.

Such substances are very dangerous from an insurance point of view, inasmuch as they may remain for days or weeks in a burning state, without this condition becoming apparent; moreover, they require such a small amount of oxygen to continue glimmering, that even tightly rolled materials may be consumed right through in this way.

The chief of these substances are tinder, touch paper, materials impregnated with saltpetre (Chili bags), fibres (bales); they are termed autocombustible materials.

The heat of combustion of individual substances can be measured by certain appliances, and expressed as the amount of heat evolved; since, however, as already mentioned, the results of such determinations fluctuate considerably, it is generally preferred to estimate the combustion temperature of a substance from the heating effect it exercises on other substances.

The unit for this purpose is the calory or heat unit, being the amount of heat necessary to raise the temperature of unit mass (1 gram or 1 kilo. of water) from an initial temperature (zero Centigrade) through *one* degree of the thermometer scale.

A distinction is drawn between the large (or technical) calory = Cal., and the small (or chemical) calory = cal.

A Cal. (kilogram calory) raises 1 kilo. (1000 grams) of water from 0° to 1°.

A cal. raises 1 gram of water from 0° to 1°.

The statement that the complete combustion of 1 gram of carbon (to carbon dioxide) furnishes 8080 cals.; of hydrogen, 34,460 cals.; of fat, 10,907 cals.; and of coal, 7500 cals., implies that 1 gram of

Carbon is capable of raising the temperature of 8080 grams of water 1° C.

Hydrogen	"	34,460	"	"
Coal	"	7,500	"	"
Fat	"	10,947	"	"

Although in connection with fire insurance practice comparatively little importance attaches to the expression of heating values in calories, nevertheless a few of these values are given below, in order to show the approximate amounts of heat disengaged by the combustion of certain important substances. It must, however, be stated that a considerable divergence exists between the reports furnished by different observers.

	calories.		calories.
Wood, green.	1,300-1,700	Wood charcoal	8,080
Wood, air-dry	3,200-4,000	Naphthalene.	9,285
Tan, pressed.	1,300-1,900	Petroleum	10,500
Peat, air-dry.	3,000-4,000	Turpentine oil	10,836
Lignite.	1,900-3,300	Paraffin.	11,140
Briquettes	400-5,200	Ethylene gas	11,858
Coal	5,000-8,000	Methane (marsh gas)	13,063
Coke	7,000-8,000	Hydrogen	34,460

## FIRE AND EXPLOSION RISKS

	calories.		calories.
Camphor . . . .	1,413	Alcohol . . . .	6,850
Sulphur . . . .	2,200	Aluminium (powder) . . . .	7,140
Carbon monoxide . . . .	2,403	Tallow . . . .	8,370
Sulphuretted hydrogen gas . . . .	2,741	Ether . . . .	9,430
Carbon disulphide . . . .	3,400	Fat . . . .	9,500
Cellulose from wood wool . . . .	4,100-4,200	Olive oil . . . .	9,800
Wood spirit (methyl alcohol) . . . .	5,370	Wax . . . .	9,000-10,000
Phosphorus . . . .	5,964	Oils, various . . . .	9,300-11,000
Magnesium wire . . . .	6,080		

For the calorific value of the various illuminants, see *Lighting*.

Combustion, in the chemical sense, is accompanied by one of three phenomena, viz. either :

- (1) By flame (flaming combustion),
- (2) By incandescence without flame (glowing combustion), or
- (3) By an absence of either flame or incandescence (non-luminous combustion, slow combustion).

All cases of combustion have one point in common, namely, the disengagement of heat, manifested by the development of a high or low temperature, according as the combustion proceeds rapidly or slowly; in the latter event, the rise in temperature is often barely appreciable, and there is neither smoke, flame, nor glow.

(1) **Flaming combustion** is usually rapid, and accompanied by a quick disengagement of heat; in the case of gases or vapours, sufficiently mixed with air, the flaming combustion may occur instantaneously, and is then called an *explosion of gas*. This may also happen with solid substances that consist to some extent of compressed gases and contain enough oxygen (see *Explosives* and *Blasting Materials*). With few exceptions, substances are incapable of exploding (as a general thing) unless they contain within themselves a sufficiency of oxygen, and can only undergo combustion provided they are furnished with the necessary oxygen by the air or by a carrier of oxygen.

Nearly all instances of flaming combustion in solid substances represent the combustion of one or more gases or vapours, which have first to be liberated by the substance in question, partly by the heat of combustion and partly by the decomposition of the substance itself. Hence the flaming combustion is merely a gaseous combustion, whereas the solid constituents of the substance are mostly only capable of glowing, e.g. carbon and wood charcoal merely glow; and if the incandescent carbon be actually surrounded by a flame, this latter merely represents the combustion of the gas, carbon monoxide, formed by the glowing carbon and atmospheric oxygen.

The flame of combustion is either accompanied by a manifestation of light or not, i.e. is either luminous or non-luminous. It would be highly erroneous to assume that every flame is necessarily also a luminous phenomenon, just as it is fundamentally inaccurate to identify every manifestation of light with flaming combustion. The flame of alcohol—and, under certain circumstances, that of gas as well—may burn without luminosity, and invisibly.

Whilst the flameless incandescence of certain solid substances is to be regarded more as a physical process, flaming combustion may be characterised as the manifestation of a chemical combination between gases, occurring without luminosity so long as the gases are pure, and

burn by themselves alone, with a sufficient supply of oxygen; on the other hand, the phenomenon is luminous when a solid body, of a refractory or incombustible character, is introduced into the atmosphere of combustion, when, for example, other substances, such as dust, burn at the same time, or, finally, when the supply of oxygen is deficient. In the latter event solid substances, mostly carbon compounds, are deposited from the gases, which substances, being raised to incandescence by the heat, produce luminosity.

As a rule the most brightly luminous cases of flaming combustion liberate the smallest amount of heat; the less visible a flame, the hotter it can be, since the combustion is more perfect; in fact, it may be asserted that up to a certain extent the temperature of a flame stands in inverse ratio to its illuminating power. Of course, the size of the flame is an important factor; the larger it is the less perfect the combustion, the smaller the liberation of heat, and the lower the intensity of the temperature.

Consequently, large illuminating flames, when burning free, are always less hot than small and less visible ones; the flame temperature of the latter most closely approximates to the temperature of combustion, even though never actually reaching it.

The reason for this fact, that flame temperature is always lower than the temperature of combustion, is to be found in certain peculiar chemical processes, a kind of auto-consumption going on within the atmosphere of the flame, which exhibits considerable variations of temperature in different parts according to position.

According to Lewes, the flame of a Bunsen burner exhibits the following differences, amounting to as much as  $447^{\circ}$  C., in various luminous and non-luminous portions of the same :—

	Flame.		Difference.
	Luminous.	Non-luminous.	
	Degrees C.	Degrees C.	Degrees C.
12 mm. ( $\frac{1}{2}$ inch) above the burner . . . . .	135	54	- 81
36 mm. ( $1\frac{1}{2}$ inch) above the burner . . . . .	421	175	- 246
Apex of the inner cone of flame . . . . .	913	1090	+ 177
Centre of the outer cone of flame . . . . .	1328	1533	+ 205
Apex of the outer cone of flame . . . . .	728	1175	+ 447
Side of the outer cone of flame . . . . .	1236	1333	+ 97

The following instances may serve as examples of certain flame temperatures, which are naturally subject to considerable fluctuation, and which can be largely modified by various means (construction of the burners, preliminary heating, &c.), namely, the flames of—

	Degrees C.
Stearin candles . . . . .	640-940
Petroleum lamps . . . . .	780-1030
Alcohol of 0.822-0.912 sp. gr. . . . .	up to 1180
Sulphur . . . . .	1820
Carbon disulphide . . . . .	2195
Coal gas (according to the kind of burner) . . . . .	900-1340
Firedamp (pit gas) . . . . .	3042

(2) **Combustion with incandescence, but without flame** is, in the case of certain substances only, a true combustion accompanied by chemical reactions, but is otherwise a merely physical phenomenon; in both cases it is accompanied by intense luminosity, the colour of which is dependent on the temperature (*incandescence temperature*) to which the substances have been heated.

Bodies may burn with both physical and chemical incandescence simultaneously; a piece of glowing iron affords an example of a purely physical luminosity, but if the iron be in the form of powder, obtained by the reduction of ferric oxide in a current of hydrogen, it will, on exposure to the air, immediately glow, and at the same time ignite spontaneously, actually burning in the air with intense incandescence (pyrophoric iron), to form an entirely different substance, viz. ferric-oxide. Carbon and antimony also are capable of physical incandescence and chemical combustion.

The incandescence of sparingly volatile, refractory, or incombustible substances is accompanied by various colour effects according to the temperature. These colorations commence with dull red heat, and pass over into light red, yellow, and finally white heat. A blue heat is also spoken of as following white heat, and a grey heat anterior to red heat.

According to the German Physico-Technical Institute, the various stages of this phenomenon occur at the following temperatures:—

A substance exhibits—

	Degrees C.
Incipient red heat . . . . .	at 525
Dark red heat . . . . .	„ 700
Cherry red heat . . . . .	„ 850
Pale red heat . . . . .	„ 950
Yellow heat . . . . .	„ 1100
Incipient white heat . . . . .	„ 1300
Full white heat . . . . .	„ 1500

According to Howe, the first faint redness appears at 475° C.; but others assert that the first emission of light occurs at dark grey heat, which, in the case of platinum, is attained at 390° C.; gold, 417° C.; and sheet iron, 377° C.

The above classification does not, of course, apply to all substances. Not a few metals arrive at the stage of white heat below 1300° C., namely, the rare metals zirconium, lanthanum, and yttrium, as also alumina, and the metals employed in the production of mantles for incandescent gas lights. Consequently, these illuminating substances do not acquire the usual white-heat temperature of 1500° C.

The carbon filament of a 16-candle glow-lamp commences to become visible under the influence of a current of 0.05 ampere and a tension of 13.07 volts.

(3) **Non-luminous combustion** is a characteristic of certain chemical reactions, which proceed quietly and slowly, without external glimmer or appreciable liberation of heat, mainly in the interior of organic substances. The general course of these reactions is similar to that of true flaming and incandescent combustion, and they furnish the same final products, but differ in their extreme slowness, and occur without any external excitation, *i.e.* spontaneously, as the result of antecedent inter-

nal natural processes of decomposition. With this kind of combustion are classed all processes of decay, and all such as are intimately connected with the so-called spontaneous ignition, under which heading they will accordingly be described. That, however, they may develop into cases of true combustion, accompanied by flame and incandescence, provided the conditions be favourable to this course, has been practically demonstrated in numerous instances.

## CHAPTER III

### SPONTANEOUS IGNITION

UNDER this heading are generally classed all cases of quick or slow oxidation or combustion brought about by chemical, electrical, biological (bacterial), or physical processes (vibration, pressure, shock, or friction) only, without the conjoint assistance of extraneous sources of heat (flame, hot or glowing bodies).

Many instances of spontaneous ignition are preceded by spontaneous heating, as a kind of prelude; others occur suddenly and even explosively, without this preliminary, so that they might be regarded as cases of spontaneous explosion. These latter, which one might term *acute* cases, are not of a more dangerous general character than such as are preceded by gradual spontaneous heating, and might, on that account, be classed as *chronic*.

Most of the substances liable to acute spontaneous ignition are well known, and the danger they entail is recognised; so that, forewarned being forearmed, one is able to take the necessary precautions and steps to except these materials from insurance, to isolate them, &c. On the other hand, with substances liable to chronic spontaneous ignition, one can never be sure; they may be stored in large quantities for years, and may be worked up, packed, and shipped without manifesting any sign of their dangerous character, until one day it is suddenly found that the mass has become internally carbonised, calcined, or entirely consumed. It is in this behaviour that the greatest danger from such cases of spontaneous ignition lies.

The process of spontaneous heating, to which the most earnest attention should be devoted, since it may at any time develop into spontaneous ignition, may best be represented by the following experiment:—

Some cotton wool is wrapped round the bulb of a thermometer, and the instrument is then introduced into a bottle containing a small quantity of some liquid that emits vapours at the ordinary temperature. The thermometer is not immersed in the liquid, but is merely suspended above the latter for some little time, whereupon it will be found that the mercury begins to rise; thus, in the case of liquid ammonia, the temperature will generally rise from, say, 10° C. at the outset to 14° C., 16° C., or over.

The cause of this accession of temperature, independent of any external incitement, is the condensation of the ammonia vapour on the fibres of the wadding; condensation of gases, vapours, or mist on porous,

fibrous substances being always accompanied by a liberation of heat. When the thermometer is drawn out of the bottle and exposed to the air, so that the vapour can escape from the cotton wool, the mercury falls again, because vaporisation is attended with loss of heat.

Under specially favourable conditions, such accessions of temperature often proceed to great lengths, and may lead to spontaneous heating, followed in turn by spontaneous ignition.

Spontaneous heating or spontaneous ignition has been already observed in practice to occur with the following substances:—

Coal, lignite, briquettes, coke, lampblack, carbonised peat;

Wood, sawdust, dye-woods, wood charcoal, cork dust, insulating materials, leather;

Colours, varnishes, resins, lacquers, oils, driers, fats, disinfecting powder, lacquered substances, oilcloth;

Fire-lighters, matches, gas-purifying materials, soda residues, slag heaps;

Metallic powders, drill turnings, burnt lime, carbides, carriers of oxygen;

Nitric acid, nitro compounds, and sulphur compounds;

Artificial manures, stall manure, fish guano, superphosphates;

Hay, clover, grass, malt, malt culms, cereal grains, bran, hops, tobacco, seeds, concentrated fodder and mixtures of same;

Wool, cotton, silk, flax, hemp, jute, tow, rope;

Oil rags, greasy cloth, polishing rags, polishing discs (buffing wheels), articles of clothing in a greasy and dusty condition.

Table D in the Appendix gives a list of the various substances which are either themselves capable of spontaneous ignition or may become so under certain exciting causes.

The processes and conditions which may incite to spontaneous heating or spontaneous ignition, taken in the widest sense, are—

		Predominantly in the case of
1. Moisture . . . . .	} Agricultural products, fodder, manures.	
2. Bacterial activity . . . . .		
3. Germination . . . . .		
4. Storage in large heaps . . . . .		Agricultural products, coal, tobacco, oleaginous substances.
5. Protracted drying . . . . .		Wood, organic substances.
6. Contained sulphur . . . . .		Lampblack, coal.
7. Contained finely divided carbon . . . . .		Metallic sulphides.
8. Contained fat or oil . . . . .		Organic substances, fibres, colours (paint), clothing.
9. Occlusion of oxygen . . . . .		Coal, &c., metals.
10. Absorption of moisture . . . . .		Quicklime, potassium, sodium, carbides.
11. Fineness of division . . . . .		Metals, bronzes, varieties of dust, fats, oils.
12. Recent calcination . . . . .		Carbonised substances, metallic powders, metallic sulphides, lampblack.
13. Exposure to the sun . . . . .		Phosphorus in fragments, oxyhydrogen gas.
14. Concentration of the sun's rays (burning glasses, lenses, glass bricks)		All readily ignitable substances.
15. Friction, pressure, shock, fall . . . . .		Numerous detonating, explosive substances (spontaneous ignition being here generally modified into explosion).
16. Electricity (sparks) . . . . .		Explosive vapour mixtures, dry cleaning works, resinous bodies.

Predominantly in the case of

- |   |  |
|---|--|
| 17. Air . . . . .                               | Phosphuretted hydrogen, and numerous compounds (ethyl-, methyl- and propyl-compounds), pyrophorous substances. |
| 18. Contact with spongy metals (platinum black) | Hydrogen gas, oxyhydrogen gas, coal gas.   |

The examples numbered 1-9 mostly exhibit slow development (chronic spontaneous ignition), those numbered 10-14 progress with moderate rapidity, whilst 15-18 are sudden and of explosive character (acute).

The period of development in cases of chronic spontaneous ignition may extend over two or three months; in many cases a good deal depends on the bulk of the stored mass; where this amounts to some hundreds of tons, as in the case of bran, cereals, &c., spontaneous ignition may sometimes take two to three months before becoming apparent externally.

Substances liable to acute spontaneous ignition are generally termed pyrophorous, and one of the most characteristic members of the group, potassium sulphide, is specially named "pyrophore."

No sharply defined classification of the kinds of spontaneous ignition is possible, the phenomenon being attended with special features in the case of almost every different substance, and also subject to considerable modification according to circumstances. The capriciousness of the phenomenon can be most clearly ascertained by experiments in the production of artificial spontaneous ignition, the results proving negative in the majority of instances, whilst in others characteristic spontaneous ignition will unexpectedly occur. For this reason the results of such experiments are never quite decisive, or at least one should never conclude from a negative experimental result in these cases that spontaneous ignition is impossible under similar conditions in practice.

For practical instances of spontaneous ignition the reader may be referred to Professor Hapke's interesting work on this subject, *Die Selbstentzündung*, which also details the progress of numerous recorded instances of this class of phenomena.

From many of these instances it is apparent that attempts to render the progress of spontaneous ignition dependent on the fulfilment of this or that condition are nugatory. The prevailing conditions are uncontrollable, and cannot be made to conform to definite rules; above all, fire insurance and other officials must be cautioned to avoid the idea that spontaneous ignition can be rendered possible or impossible by the non-fulfilment, or the reverse, of one or more conditions.

For the occurrence of spontaneous ignition in organic bodies at a low temperature, the following are a few of the essential points: presence of some carbonaceous, combustible substance, moisture, oxygen, and a certain minimum temperature.

It must be admitted that these requirements are applicable to many conditions, just as it is undeniable that, in order to warm and illuminate a cold, dark room, the employment of a stove, fuel, lamp, and also fire is necessary; but to endeavour to correlate these requirements to *all* conditions is inadmissible, since, in the case of fibrous materials impregnated with oil, for example, moisture, so far from being essential, actually retards the progress of spontaneous ignition, oily rags being capable of spontaneously igniting only when in a dry state.

Beams of timber may become capable of spontaneous ignition when exposed to the prolonged influence of moderate warmth, even below  $100^{\circ}\text{C}$ ., but not until the whole of the moisture has been driven off; thus accomplished, a warmer current of air is all that is necessary to cause them to take fire of themselves.

The sole idea that these few examples are intended to convey is that the general prevention of spontaneous ignition by adherence to cut and dried regulations is unattainable; furthermore, that no Insurance Company should allow itself to be persuaded that any substance which has already proved in practice to be attended with the risk of spontaneous ignition can be considered as freed from that risk by the adoption of special conditions.

With regard to the spontaneous ignition of various substances, the reader is referred to the paragraphs dealing with those substances.

Fires produced by the influence of the sun's rays must be regarded as a species of spontaneous ignition. These fires and explosions are so much the more important in that they frequently occur in cases where least expected; and they consequently deserve to be dealt with separately.

**The Sun as an Incendiary and Cause of Explosions.**—That in many cases of fires of doubtful origin the sun has largely contributed, and may have, or indeed has, been the exciting cause, is an assumption that should not be hastily rejected, numerous fires having been actually traced to the action of the luminary. Le Chatelier estimates the solar temperature at  $7600^{\circ}\text{C}$ .

To call attention, more closely than has hitherto been the case, to this insidious action of that remote body, the sun, and at the same time to ensure greater precautions being taken against the dangers of the sun's rays, the principal factors in this connection are given below.

(1) The sun's rays when focussed to a point through a lens are, by reason of their intense heat, able to carbonise and ignite organic substances in a very short time.

Lenses and burning glasses may be replaced for this purpose by any glass article, *e.g.* glass bottles, glass balls, glass vessels, stand glasses, spectacle glasses, optical and photographic lenses, glass tiles, and all defective glass articles containing air bubbles.

In this latter case the air bubble acts as a lens, and focusses the rays. Glass tiles have proved specially dangerous, particularly when placed in roofs over lofts containing dry hay, straw, &c. When the only means of lighting such places is through the roof, it is better to employ plain sheet glass, free from air bubbles, and painted over with a mixture of white lead, varnish, and oil of turpentine.

(2) When water containing even only traces of explosive salts or fulminates is dried, the residual patches of dry substance will be exploded spontaneously by the slightest insolation.

(3) Dry nitrogen chloride, nitrogen fluoride, and nitrogen iodide (the latter also in the wet state) will explode directly they are exposed to the sun's rays.

(4) A mixture of chlorine and hydrogen explodes in sunlight.

(5) Igniting pellets (*q.v.*) for fireworks explode when exposed to direct sunlight for several hours.

(6) *Large* lumps of phosphorus ignite in sunlight.

(7) Chlorine gas and methane (marsh gas) explode when mixed together and exposed to the sun's rays for some time.

(8) Mixtures of chlorine and acetylene explode with great violence in sunlight.

(9) The same remark applies to a mixture of chlorine and vinyl hydride.

(10) Glass vessels containing dangerous liquids (benzine, ether, carbon disulphide) may burst on prolonged insolation, the escaping liquid becoming ignited in contact with any adjacent flame. Furthermore, the vapours of the heated contents are liable to take fire or explode if mixed with air.

(11) Vessels containing bleaching powder are burst by the sun's rays in consequence of the liberation of oxygen effected by the heat.

(12) All liquefied gases and vapours stored, under pressure, in steel vessels attain such a high tension on prolonged insolation as to burst the vessels with violence. The extent to which the internal pressure is augmented by insolation can be gathered from the case of ammonia gas (liquefied), the tension of which is 4.4 atmos. at zero C., 7 atmos. at 15° C., 10 atmos. at 28° C., and 15.3 atmos. at 40° C., to which latter temperature the vessels can easily be raised by a few hours' exposure to the summer sun.

(13) The dried fibres of hemp, flax, jute, tow, as also hay, straw, and similar substances, very readily take fire spontaneously when they are stored in lofts, directly under the roof, so tightly that ventilation of the surface is precluded; under these conditions two or three weeks' constant dry weather will suffice to convert the substances in question into a mass that carbonises and ignites spontaneously.

(14) When carbon disulphide containing dissolved phosphorus is sprayed and vaporised, the residual traces of phosphorus ignite on exposure to sunlight.

(15) The prolonged exposure of ether to sun and air leads to the formation of vinyl alcohol, which may cause serious spontaneous explosions on the evaporation of the ether (*q.v.*).

(16) Barrels filled with tar can be exploded by sun heat, if the tar still retains its readily volatile constituents.

(17) The solar rays foster the processes of spontaneous ignition and heating, by retarding superficial cooling, and, moreover, themselves exert a heating effect on such surfaces.

(18) These rays will sublime naphthalene and camphor; and the penetration of the resulting vapours into porous materials renders the latter inflammable.

## CHAPTER IV

### EXPLOSIONS AND EXPLOSIVE SUBSTANCES

THE term "explosive" is applied, in a chemical sense, to such solid or liquid substances as possess the faculty, under certain circumstances, of undergoing instantaneous decomposition, extending throughout their entire mass and accompanied by a considerable disengagement of heat,

the substance at the same time being partly or wholly converted into gaseous decomposition products.

Solid and liquid explosives represent gases or vapours condensed into the smallest possible compass, in the solid or liquid form.

The substances used in the arts for blasting are termed "explosives" or "blasting materials."

The phenomenon of explosion is a sudden and enormous expansion of gases and vapours liberated from a previous condition of chemical combination.

Certain gases or vapours are also termed explosive; but this is a quality they mostly do not possess so long as they are pure, unmixed, and under ordinary pressure; and they only acquire it on being mixed with air, other gases, vapours, floating particles of solid dust, in certain proportions by volume, or when they are liquefied, solidified, or in any way exposed to high pressure, in which latter event they may, even in an unmixed condition, give rise to violent explosions (gas or dust explosions).

Finally, also, the term explosive is applied to apparatus, vessels, Montejus apparatus, conduit pipes, shafts (see *Alum*), machine parts, and flywheels. In such cases it is usual to speak of boiler explosions, tank explosions, lamp explosions, stove explosions, &c., though probably with the exception of the last two named, which may be due to gas explosions, these accidents have nothing in common, chemically speaking, with the explosions already referred to, being caused not by chemical reaction, but by physical phenomena, such as weakness or defects of construction of the walls or fittings of the vessel, defects in material, rapid motion, falls, shock, &c.

Such an explosion is more a destruction or annihilation of an article than a dissociation or liberation of chemically combined elements, the materials of which these exploded articles are made (*e.g.* iron, glass, clay, or stone) being of themselves non-explosive.

A boiler is said to have "exploded" when the walls of the vessel have suffered disruption, while in work, to such an extent that a sudden equalisation of pressure between the inside and outside of the vessel occurs as a result of an escape of steam or water. Strictly speaking, such an occurrence should not be called an "explosion"; but as the term has already gained general acceptance, we will retain it here.

In describing explosives, it is first of all necessary to dispel the generally received, but fundamentally erroneous idea, that such substances are invariably and necessarily dangerous, which is by no means the case. Now, whilst it is true that Insurance Companies, officials, and mankind generally, may be very well satisfied that such an opinion should prevail; and whilst a little more respect than is absolutely essential with regard to the dangerous character of explosives may be advantageous as tending to prevent many cases of accident; still, on the other hand, this hypercautiousness may easily become excessive, and degenerate from caution into anxiety, which leads to uncertainty; and this latter only too easily induces accident, especially where the storage, treatment, handling, and carriage of little-known explosive materials are in question.

It is therefore desirable that all persons who are entrusted with the

handling of explosive substances should be made acquainted with their nature and dangerous properties, and be specially impressed with the knowledge that: *the majority of explosive substances, and especially blasting explosives, only become dangerous in this respect under well-defined circumstances and on the fulfilment of certain conditions, but not otherwise.* True, there are numbers of very capricious explosive substances, which exhibit a tendency to go off at any moment, and require to be handled with the greatest care; this applies to the fulminates (detonating salts), the fluoride, chloride, iodide, and bromide of nitrogen, acetylene chloride, perchloric acid, frozen nitroglycerin and dynamite, acetylene kept under heavy pressure or in the liquid state; but, on the other hand, various dynamites, nitro-celluloses, blasting explosives, and explosive gases, though generally classed as by no means less dangerous than the foregoing, do not actually explode except under certain definite conditions.

The safety of explosive substances increases with their purity, a factor which also influences their stability; for instance, a thoroughly purified sample of nitroglycerin (actually the *first* specimen prepared of this explosive), that has been kept in Nobel's laboratory ever since 1847, *i.e.* over fifty-four years, exhibits no decrease in explosive power in the annual tests to which it is subjected.

Little is known of the actual character of the solid and liquid explosive substances at the moment of explosion; almost every one of them behaves differently, and requires a different inciting cause: one needs to be struck, rubbed, or subjected to percussion; another has to be heated; a third brought into contact with a flame or spark; another requires to be compressed or packed; some must be in a dry state, others damp, and others again frozen, before they can be brought to explode. Some will not go off unless in an impure condition, or mixed with other, perhaps entirely harmless, substances; in fact, so many special peculiarities have to be borne in mind in connection with these explosive bodies, that no general rule can be laid down with regard to the progress of explosion in the case of liquids or solids. Consequently, every substance that is capable of producing explosions requires individual treatment in respect of storage, working up, handling, and manufacture.

Even the capacity of explosives for acting at a distance, when set off, differs considerably—exploded dynamite, for instance, being able to explode other dynamite over 30 yards away, an effect that the still more powerfully explosive gun-cotton is incapable of producing.

Apart from blasting materials, explosions have been recorded in the case of gases, vapours, fats, oils, metals, slags, various kinds of dust, fuel, numerous chemicals, resins, and vessels. Special risk in this connection is incurred:—

(1) By **inflammable gases and vapours** in blast furnaces, puddling furnaces, cupola furnaces, foundries, heating stoves, gas stoves, briquette works, slag works, lacquering stoves, boiler stokeholes, chemical works, and laboratories, dry-cleaning works, oil-cloth factories, factories where benzene, ether, carbon disulphide, or spirits are manufactured; fat extracting establishments, resin, varnish, and turpentine plant, cooperages, wood charcoal works, waste-carbonising works, gasworks, coke factories, nitrating works, ceresin works, soldering lamps, acetylene

plant, carbide works, and lighting works (*in toto*, excepting electric lighting and illumination with fatty oils); distilleries, especially those connected with alcohol, tar, and all substances giving off inflammable vapours (ether); manufactories of blasting materials, flashing substances, fire-lighters, fireworks; water-gas plant (and similar establishments); dégras factories, lubricant factories, tallow melting works, vulcanising works, patent leather works, and lampblack factories.

(2) **By explosive dust** in all kinds of mills dealing with agricultural products, cork works, wood-working establishments, plant for treating coal, drying kilns, lampblack factories, sawmills, cement mills, sugar works, maltings, grain cleaning works, silos, bronze powder factories, and metallic powder works. *starch*

(3) **By physical influences** in steam boilers, vessels containing steam, steam pipes, steam-boiling plant, cask steaming plant, gas liquefying plant, gas cylinders, acid carboy stores, motors, alloys, hollow shafts or those filled with alum, flywheels, grindstones, polishing wheels, circular saws, heating installations, and central heating plant.

### 1. Furnace Explosions

Household stoves, boiler firing appliances, and all technical stoves or furnaces (annealing ovens, puddling furnaces, blast furnaces, lime-kilns, &c.) are liable to explosion when (a) defective, (b) badly constructed, or (c) worked in an improper manner.

Where wood fuel is used (apart from wood-gas firing in glass works, &c.) the risk of explosion is small, but is greater in the case of firing with briquettes, coal, or lignite.

Stove and furnace explosions are in reality explosions of gas, partly within the stove, partly in the flues; they may be explained in the following manner:—

Complete combustion of the fuel is never attained in stoves or furnaces; in incomplete combustion the harmless carbon dioxide is always accompanied by some carbon monoxide, which is combustible and capable of forming explosive mixtures with air; in addition to which, inflammable hydrocarbons are also produced.

Mixtures of carbon monoxide and air become explosive as soon as the proportion of the former gas attains 10 per cent., and they remain so until the proportion reaches 72 per cent.; hence the limits of explosibility have a very wide range, and the risk is therefore high. That, as a matter of fact, these explosions are comparatively rare is attributable to the circumstance that the products of combustion do not consist exclusively of carbon monoxide and air, but also of the final product, incombustible carbon dioxide, and further to the fact that the bulk of the carbon monoxide burns immediately it is formed, and therefore does not really enter into the constitution of the gaseous mixture.

The danger of explosions in stoves and furnaces is mainly due to air finding its way through defective flues and fireplaces into the out-going gases, and forming with them an explosive mixture, which by contact with a flame or spark may explode either in the fireplace itself or in the flues leading to the smoke-stack.

Another cause arises when the mass of glowing fuel is so thickly

covered over with a freshly introduced quantity as to momentarily quench the fire and produce a very imperfect combustion of the materials, the result being the formation of a large amount of hydrocarbons and unconsumed carbon monoxide, the fire gases being thus enriched in carbon monoxide and impoverished in harmless carbon dioxide. Under these circumstances, when, by lapse of time or through the fire door being open or the fire stoked, the hitherto smouldering fuel is caused to flame up, the flame may overtake the mixture of gas and air in the flues and cause it to ignite; matters, however, do not always remain at this stage, an explosion ensuing when the proportion of carbon monoxide in the mixture is between 10 and 75 per cent.

The same danger is incurred when the fire doors and flues are tightly closed by dampers on stopping work, and while fuel is still smouldering in the fireplace. In such case an inflammable mixture is formed in the closed firebox, and may, by accession of air through the crevices of the door, develop into an explosive mixture, which takes fire or explodes when the fire is stirred up again on resuming work.

These phenomena are liable to occur in any kind of stove or furnace, and can only be obviated by keeping the appliances in good order (this also applies to household stoves), giving them proper attention, and employing reliable stokers who are well acquainted with all the dangers attending their use.

Every stove or furnace with defective brickwork or flues is liable to the risk of explosion, until the imperfections are remedied. Precisely similar conditions occur in metallurgical furnaces fitted with pipes for the air-blast, gas being liable to escape into the blast pipes and form explosive mixtures with the compressed air therein.

The drying stoves of briquette and suchlike factories are subject to explosions of coal dust, both when at work and when idle. The insides of these stoves are coated with very finely divided coal dust, which is dislodged and disseminated through the internal air by any operations performed in the stoves, and consists of readily inflammable hydrocarbons in addition to solid carbon. The slightest ignition may produce an explosion; and practical experience has shown that in the course of carrying out repairs the fall of a hammer may lead to the destruction of the stove by an explosion, probably caused by a spark consequent on the hammer striking against the iron fittings (see also *Dust Explosions*).

Explosions in puddling furnaces may be caused by cooling down the hearth with water; the contact of the water with the still glowing masses of slag may not only suddenly liberate large volumes of steam, but also form hydrogen or oxyhydrogen gas (*q.v.*) by the action of the glowing materials (iron, slag) on the steam produced.

These puddling furnace explosions, therefore, generally occur in two stages: the first explosion being due to the expansive force of the liberated steam, and the second explosion ensuing on the formation and ignition of oxyhydrogen gas.

Blast furnaces incur risk of explosion through the scaffolding, or irregular descent of the charge, the result of which is to form cavities among the materials (carbon, iron ore, and fluxes) composing the charge. When the scaffolding suddenly falls, an irruption of air may ensue, which forms with the blast-furnace gases (rich as these are in hydro-

carbons and carbon monoxide) an explosive mixture that may ignite by contact with the glowing charge, or be heated to explosion point by the high temperature of the furnace.

These obstructions may be formed in two ways: one by the furnace getting too *cold* (puddling, Thomas, and steel furnaces); the other by *overheating*, which more frequently happens in blast furnaces. No type of blast furnace that will entirely prevent the hanging of the charge has yet been discovered.

Blast-furnace gases are largely used for heating the blast (see *Water-gas*); they are themselves not of a dangerous character, and when alone rarely, if ever, explode. On this account it has also been assumed that such explosions are not so much due to the gas as to the dust, *i.e.* the thick dust given off by the descending coal.

Sometimes blast-furnace explosions are due to the formation of other gases. Whereas blast-furnace gas, consisting on the average of about 5 per cent. of carbon dioxide, 23 per cent. of carbon monoxide, 12 per cent. of water vapour, and 60 per cent. of nitrogen, is not of very dangerous composition, other gases are better adapted to produce violent explosions. For instance, oxyhydrogen gas may be formed in consequence of water trickling in through defective parts from the cooling plant on to the compact glowing metal, the result being a violent explosion. Again, during the tapping of the furnace and removing the slag, inflammable gases, rich in carbon monoxide, may escape and explode.

Similarly, explosions may also occur by accession of air into the pipes drawing off the furnace gas; they are, however, free from danger, since the conduits are fitted with effectual explosion valves, which permit the detonation of an explosive gaseous mixture even within the pipes.

Explosions occur in lime kilns, gypsum furnaces, &c., when the flues are too narrow, or are so choked up that the products of combustion cannot pass away fast enough, but collect in the furnace and become so strongly heated by contact with the glowing stone, or ignited by flame, that they finally explode.

## 2. Metal Explosions

Foundry explosions are mostly due to the molten metal coming in contact with water, which is thereby decomposed, no matter what its condition, into its constituents, oxygen and hydrogen. These two gases, when merely in a condition of mechanical admixture, form the highly explosive oxyhydrogen gas (see *Oxyhydrogen Gas* and the respective metals), which readily ignites in contact with the glowing metal. These explosions are of a very violent character.

The metals attended with special danger in this connection are iron, cobalt, manganese, bismuth, tin, and magnesium.

Light metals, such as potassium, sodium, calcium, strontium, barium, and rubidium, can also decompose water in a similar manner, without, however, first needing to be in the molten state (and therefore at moderate temperatures), and will produce analogous explosions; a few metals require the water to have attained a temperature of 30, 60, or 100° C. (see *Bronzes, Metals*).

Like the metals, glowing slag is able to produce explosions of all kinds when brought into contact with water. In this case, however, as experience in Luxembourg has shown, still another factor comes into play, namely, that the slag contains inclusions of gas in its cavities, which gases are partly formed in the slag blocks themselves, and are therefore under high pressure. When such blocks are cooled with water (or even by the winter air) the mass contracts, thereby increasing the pressure on the imprisoned gases, which then often burst the blocks. All these explosions are of very violent character.

Explosions of metallic alloys, also, have occurred of very peculiar nature, and for which no sufficient explanation has yet been discovered. To this class belong certain explosions of rhodium-lead alloys (1:2) occurring on exposure to the heat of a gas flame. Perhaps an important part in this phenomenon is played by the moisture which rhodium (like palladium) occludes in large quantities.

Explosive phenomena have also been manifested, in the case of the antimony film deposited on copper by electrolysis, on bending the copper, or subjecting the layer to friction, percussion, or shock.

Strictly speaking, it is erroneous to talk of explosions of metals, since the mass of metal does not explode, but simply originates the substance which gives rise to the explosion. The expression is, however, in such general use that it has been retained here.

### 3. Machinery Explosions

Machines and machine parts are also subject to so-called explosions, which, though not the direct cause of fires, must, nevertheless, be briefly mentioned here, since, owing to their possibly destructive effects on gas pipes, steam pipes, vessels holding dangerous liquids, lighting plant, &c., they are highly important in connection with fire insurance.

On this account it is desirable to bestow attention on the condition, character, and working of industrial mechanical appliances. The age, state of repair, and maintenance of the machinery, the nature and frequency of the inspection to which it is officially subjected, and the high requirements imposed on machinery which is very often defective, all form very valuable factors in judging the general fire risk. Frequently repaired flywheels, centrifugal machines, and quick-running machine parts should all be regarded with a certain distrust.

In the case of power-driven grindstones, it should be noted whether the same are fitted with wooden axles, which, under the influence of the water used on the stone, may swell up to such an extent as to burst the quick-running stone itself; several cases of this kind have been known to do a deal of damage. Another cause of similar mishaps is by one part of the stone becoming thoroughly soaked with water, by prolonged immersion, whilst the remainder is quite dry, the consequence being that the wet part is heavier than the rest, and will tend to attain a greater velocity when running at high speed, thus causing jolts, and ultimately leading to its flying to pieces, *i.e.* exploding.

Special danger attaches to grindstones that have been patched, chipped in places, or worn out of true. For axle explosions, see *Alum.*

Similar conditions prevail in the case of flywheels; only here the danger is far greater, owing to the immense size of some of them (up to

30 feet in diameter, weighing 40 tons, and running at a velocity of nearly 90 feet per second).

Flywheels in work must always be looked upon as loaded bombs, capable of going off explosively if run above the maximum permissible speed, which may easily occur should the engine run away in consequence of careless driving.

Flywheels have also been known to burst or explode when running at normal speed, without the accident being traceable to any external cause; prolonged use (20–25 years), almost inappreciable distortion of individual parts of the wheel caused by the constant reciprocal reaction between rim and spokes, slight displacement, sinking of the bearings, the shaft getting out of true, defects in the metal—all these possibilities may induce highly dangerous “explosions,” which necessitate the introduction of special fire insurance regulations with respect to the position of the engine in relation to particularly risky portions of the installation (lighting plant, steam plant, tanks and stores for dangerous substances, &c.). These conditions have special reference to ensuring that no plant, the destruction of which might cause danger from fire, is in the most likely path that would be traversed by heavy flying portions of broken machinery in the event of such an accident.

Flywheels rotating on a line with plant liable to risk of fire or explosion are always a possible source of danger to the latter.

For particulars respecting explosions of compressors, steam cylinders, &c., see under *Lubricants*.

#### 4. Explosions of Tanks and similar Vessels

The working and control of all kinds of vessels that contain steam are already so stringently regulated by administrative enactments, as to render their discussion in this place superfluous; and we will therefore confine ourselves to a brief mention of the numerous Montejus apparatus, autoclaves, digestors, and similar vessels employed in factories where pharmaceutical preparations are made, which vessels are mostly exposed to severe strain, oftentimes patched, and frequently in a very dilapidated condition.

Not infrequently these vessels are unprovided with the necessary safety-valves, and also the no less important tap for blowing off steam to reduce the pressure before the cover or manhole is opened. The premature removal of a cover or manhole fastenings, while the vessel is still under half pressure, has led to numerous explosions; and the danger is still greater and more directly attended with fire risk when the vessel contains inflammable liquids, such as alcohol, benzine, ether, carbon disulphide, wood spirit, or acetone, the danger of ignition, to say nothing of that of flameless explosion, being then particularly imminent.

Metal vessels and apparatus lined with lead to prevent corrosion by the contained acids or lyes frequently exhibit blistering of the lead. This is due to the percolation of small quantities of the contents through defective parts of the lining, the underlying metal being attacked, and gases (principally hydrogen or oxyhydrogen gas) formed, which thrust the lead outwards.

In repairing these defects, care must be taken to avoid striking the blistered spots, and the use of soldering lamps or other open lights must

be strictly prohibited; otherwise, explosions of great violence may occur. The vessels must always be well ventilated before repairs are commenced.

In one very serious instance of this kind, the workmen, who were using an open soldering flame in the tank, were literally sheathed in the lead blown out by the explosion, and the metal had to be cut away in pieces to reach the two bodies.

Equally liable to explosion are *all* vessels and casks that have contained liquids giving off inflammable vapours. The residues of the liquid evaporate, and the vapours form explosive mixtures with the air in the vessel—in the course of a couple of days, whether the vessel is open or closed. These explosions, which may be induced by the introduction of a naked light, a violent blow, or a spark, are extremely violent and igniting.

Moreover, mention must also be made of explosions of barrels and tanks which are only steamed out at intervals, or are lined internally with resinous materials or pitch (see *Breweries*).

The explosions occurring during the steaming, cleansing, or disinfecting of tanks and other vessels result from the employment of steam at a momentarily excessive pressure, or in consequence of defective structural material. Such explosions never give rise to flame when they happen in fireproof localities. On the other hand, the explosions arising in the pitching of casks, &c., are mostly attended with considerable flame, and liable to cause fires.

The materials used in **cask pitching** are of two kinds:—

(1) The pitch (shoemaker's, ship's, or cask pitch) obtained from coal-tar or resin; (2) cask lacquer (fluid pitch, brewer's varnish), composed of shellac, colophony, wax, turpentine, and spirit.

Before use, the pitch must be melted, and the lacquer dissolved in spirit; in both cases the risk of fire is by no means small. The melting of pitch leads to the formation of inflammable vapours (see *Tar and Resin*); the mass easily boils over, and is then liable to take fire. In pouring the pitch out over the inner walls of the vessel, the liberation of inflammable vapour is still more extensive than before, owing to the larger surface presented by the mass; this vapour mingles with air and forms gaseous mixtures that are both inflammable and explosive, and may lead to highly dangerous explosions when brought into contact with the glowing iron usually introduced into the vessel for the purpose of burning it out. This operation should always be performed in a fire-proof locality, and at a distance of at least ten yards from any inflammable object.

Many experts attribute these explosions to electrical excitation, to which pitch—containing, as it does, a large proportion of substances (turpentine oils) volatile below 392° F.—is particularly prone.

The preparation and application of cask lacquer is also dangerous, though not in such a high degree, so far as explosion is concerned, as the operation just described. The aforesaid inflammable ingredients require to be dissolved in alcohol with the aid of heat; and, since the application of the hot solution liberates a quantity of explosive hot alcoholic vapours, this operation also must be performed in fireproof localities, and without the assistance of fire or flame.

Mention may here be made of explosions of coffee machines operated

by steam pressure; these must be regarded as small steam boilers, and are generally heated with petroleum, spirit, or direct fire. The steam pressure in this case is not high, though, as practical experience has shown, it may lead to serious damage when the apparatus is situated in a risky part of the establishment, conflagrations then ensuing, less owing to the explosion of the apparatus itself than to the burning of the fuel scattered about by the explosion. These explosions are usually caused by obstructions in the filter, or by omission to extinguish the heating flame in proper time.

### 5. Explosions of Soldering Lamps, &c.

To this class belong soldering and brazing lamps, and similar appliances (smithy forges). Those in common use in glass and metal works are attended with manifold risks: they are dangerous in themselves, owing to their liability to explode; additional risk arises from the chance of igniting inflammable materials, owing to the high temperature of the flame; finally, there is an indirect danger of explosion, due to the necessity of keeping and storing a stock of readily inflammable and eventually explosive fuel.

Soldering and blowpipe lamps are more dangerous than a real forge, because they can be carried about or overturned, and because the workmen are not always sufficiently careful in the choice of the positions into which they bring the still flaming lamps. This rarely, if ever, happens in the case of forges, which are mostly fixtures, can hardly be upset, are difficult to transport, and are (or rather always should be) provided with a fireproof cover of stone or metal, and with a brim to prevent the escape of spilt and burning materials.

The danger of lamp work is further augmented by leaving the still blowing lamp in any place. A benzine soldering lamp of the newest type (fed with about 10 ozs. of benzine) will continue to burn for two to three hours, and the high temperature of the flame ( $1000^{\circ}$  to  $2000^{\circ}$  C.) may set fire to materials that are not quite flameproof at some distance away, when the flame is allowed to continue playing in one place.

Since both kinds of lamp are liable to explode, no matter what material is used, it is desirable to enjoin that the material and fittings (of portable lamps especially) should be of the best, brazed, and provided with a safety-valve in the filling-cap. The same requirements as to quality should be exacted of the fuel, which must at least be technically pure; the wicks should be changed frequently, since fouled wicks readily lead to explosions (see *Lighting*).

The fuel employed, for soldering lamps in particular, includes benzine, petroleum, gasoline, hydriine, spirit, and coal gas. The same are also used for forges, though for this purpose more frequent use is made of paraffin, train oil, tallow, or petroleum, which generate far less heat than those mentioned above. In petroleum blowpipes the temperature is about  $1300^{\circ}$  to  $1400^{\circ}$  C., but in other cases it is  $1000^{\circ}$  to  $2000^{\circ}$  C., greater heat being unattainable unless use is made of the oxyhydrogen jet or other similar gases, which will give temperatures as high as  $2840^{\circ}$  C.

According to the fuel employed, the material is either first gasified by a preliminary heating, followed by combustion of the vapour in admixture with air (blowpipe and soldering lamps fed with benzine,

spirit, gasoline, or hydriding); or the combustion is effected direct, without previous gasification, by the aid of a wick and a powerful supply of air blown into the flame, which thereby attains a high temperature (forges fed with paraffin, tallow, wax, oil, or gas). In the latter forms of apparatus explosions may result from the (often defective) container becoming overheated (bad, carbonised wick).

The temperature required in many instances of soldering metals is far below that which the various soldering lamps are capable of furnishing, owing to the extensive use of easily fusible solders, melting as low as about  $94^{\circ}$  to  $430^{\circ}$  C.

It is necessary to mention here that soldering operations in the case of apparatus or pipes for inflammable gases (coal gas in particular, and acetylene most of all) must not be commenced until the articles under treatment have been emptied of gas. With acetylene apparatus it is essential that in addition to opening the vessel, &c., the same must be emptied by submerging and filling it with water; otherwise the gas, which has about the same density as air, will not be completely removed.

## 6. Explosions of Acid Carboys, Acid Vapours

The acids here in question are the stronger kinds only, mainly nitric acid of sp. gr. 1.350–1.530, 55–100 per cent. strength, and measuring  $37.5$ – $49.5^{\circ}$  Beaumé; and sulphuric acid of sp. gr. 1.5–1.8, 60–100 per cent. strength, and measuring  $48$ – $66^{\circ}$  B.

Explosions of acid carboys are by no means rare, nor do they depend on the nature of the acid or the material of the carboys, but may occur under almost all conditions, provided the acid be sufficiently strong.

It should be particularly noted that the gases liberated by nitric acid—the so-called nitrous fumes—consisting of nitrous and hyponitrous acids, are highly poisonous, and therefore retard the work of extinction and rescue in cases of fire. Explosions of acid may arise from four different causes:—

(1) The liberation of vapours from the acids themselves (nitric acid, hydrochloric acid, or mixtures of nitric and sulphuric acid), as the result of over warm storage, or exposure to the direct rays of the sun. The latter very often cause explosions, on which account fire insurance companies should see that the carboys are stored in a cool place, on the shady side of the factory yard.

(2) Decomposition of the acids, a matter of frequent occurrence with mixtures of nitric and sulphuric acids, especially when warm. Such mixtures have been known to burst the strongest iron vessels after having stood for a few hours in the sun, the cause being the production of nitrous fumes; the explosions are of a very violent character.

(3) The formation of hydrogen gas. This can only occur in metal vessels, not in those of glass, the metal being corroded by the acid in weak places (caused by rust or defective material), whereby hydrogen is formed, and the resulting pressure bursts the closed vessel. Risk of this kind is specially imminent in the case of metallic vessels containing sulphuric acid, when the same have stood for a long time in the sun.

(4) Violent shocks may also liberate the acid vapours from solution, and burst the vessel.

In accidents of this kind it is often noticed that the bursting of one carboy is quickly followed by the bursting of those adjoining. Such a possibility entails the provision of special precautions, which will be discussed further on.

Carboy explosions are not always or directly followed by outbreaks of fire, since they are flameless; nevertheless, they are capable of causing extensive fires when pure or mixed nitric acid is in question, the vapours of which may come into contact with organic or readily inflammable substances like coal, lignite, hay, straw, wood wool, sawdust, paper, seaweed, plants and seeds, dried fruit, fibres, textiles, packing materials, &c. All these substances are nitrated by this acid (see *Nitration*), an operation generating sufficient heat to set them on fire, besides which they may be highly explosive in the nitrated condition. Hence the danger is twofold: fire and explosion.

The behaviour of substances towards acids is naturally highly divergent; and the following results have been obtained in experiments with nitric acid of sp. gr. 1.236–1.388, and 28–41° B.

In the case of straw, acid of 32° B. and sp. gr. 1.279; and with hay, acid of 29° B. and sp. gr. 1.246; sufficed to set fire (spontaneous ignition) to the mass, though no ignition ensued in the case of weaker acid. Hay is here more readily inflammable than straw, and also than other substances, *e.g.* sawdust, which could also be ignited.

The time required for the inception of spontaneous ignition, measured from the soaking of the material with nitric acid to the actual outburst of flame, was, with acid of sp. gr. 1.30–1.388 (34–41° B.), 35–45 minutes in the case of hay or straw; with weaker acid ignition did not occur till the end of 3½ hours.

Other trials showed that straw could be fired by nitric acid of 29° B. (sp. gr. 1.246), and that the same result could be obtained with other packing materials, seaweed, &c., and even more easily on exposing them to the sun so as to acquire a temperature of 40°–50° C.

This latter risk is particularly incurred by the straw covering usually put round acid carboys; consequently, the stoppers and wrappings of these carboys should preferably consist of fireproof materials (glass, porcelain, clay, putty, kieselguhr, sulphur), the stoppers being so arranged as to allow the internal pressure to be eased when the carboys are stored full in hot weather.

This last precaution does not entirely preclude the possibility of explosions arising from the liberated acid vapours; it is essential that the vessels containing acid should have a free space inside (about 120 cubic inches), or, if received quite full, must be emptied of a small quantity (about ½ gallon) of their contents.

No large number of acid carboys should ever be stored near coal or packing materials, or indeed any kind of inflammable organic substances; and warm storage places should be avoided even for single carboys.

The wrapping and the stoppers of the carboys should be made fireproof by impregnation.

When a load of carboys is received, the stoppers should be loosened; and when the weather is warm all the carboys should be sprinkled with water immediately, in order to keep the contents cool.

No more than ten carboys should be set close together in any one spot, and even these should be arranged in one or two rows, not in a

square, with a passage way between the rows. The carboys should rest on a grating of laths, and gutters be provided in the floor, for draining off any leaking acid without bringing the same into contact with any of the other vessels.

The storage place should be shaded from the sun, and not entirely closed, but open and well ventilated. Large stocks of acid require to be kept in works of the following character: chemical factories, dynamite works, blasting explosives factories, sulphuric acid works, soda factories, metal goods works, installations where nitration is performed, gasworks, picric acid works, aniline works; and large quantities have also often to be kept in railway goods sheds, and, of course, in works where nitric acid and hydrochloric acid are manufactured.

In the event of an outbreak of fire in such stores of acid, the only means of extinction is by spraying with water from a distance, owing to the highly poisonous nature of the vapours; the use of sand, earth, ashes, tan, or sawdust must be strictly prohibited, since—with the exception of sand and earth, which may be used in large quantities, though only in the case of small fires—these substances may become a source of danger, and help to spread the fire, being themselves partly nitrated.

When a carboy bursts, the adjoining ones should be carefully removed after having been thoroughly cooled down with water, since otherwise they too might burst. A large supply of water, with the necessary utensils for lading it out, must be kept near the acid store.

In handling carboys, none but the strongest type of tippers should be used, since these alone prevent the risk of spilling the acid, enable it to be poured out carefully, and preclude the possibility of the carboys being overturned during the operation.

## 7. Explosions of Gases and Vapours

In its widest sense the term gas is applied to all (aeriform) bodies the minutest particles of which exhibit the tendency to fly apart from each other as far as possible in all directions.

In its restricted sense, however, the name gas is applied to bodies that exist in the gaseous state at the ordinary temperature and pressure, and can only be liquefied or solidified by artificial means (high pressure or great cold). To this class belong air, nitrogen, oxygen, carbon dioxide, hydrogen, carbon monoxide, chlorine, ammonia, marsh gas, acetylene, coal gas, and ethylene.

Vapours, strictly speaking, are the gases given off, with or without the aid of heat, by bodies that under ordinary circumstances are either solid or liquid, and include the vapours of alcohol, ether, benzine, carbon disulphide, and, up to a certain extent, water vapour as well (this last must not be confounded with water-gas).

Many vapours liberated from substances lighter than water are far heavier than air (with regard to the density of gases and vapours, see under *Ventilation*).

When several gases or vapours are present simultaneously in one and the same vessel, they mix with comparative rapidity; only very dense vapours and very light gases remaining unmixed for any length of time.

*Under ordinary circumstances, and when in a pure state, gases and*

*vapours are non-explosive, even though combustible.* This fact has already been briefly mentioned, and may now be illustrated by the following experiment.

If in a litre flask we heat sufficient gasoline or petroleum ether (say 40 drops) for the liberated vapour to expel all the air present and fill the flask, and the vapour be then ignited, it will burn quietly without exploding; but if the experiment be repeated with only half the previous quantity (20 drops), a little air will be left in the flask, and ignition will be accompanied by detonation. Finally, on trying again, this time with only 10 drops of gasoline, the amount of air left in the flask will be still greater; and on introducing a burning object into the flask, a sudden combustion accompanied by a loud report (explosion) will occur.

This experiment is highly instructive, and its phenomena may be explained as follows: Just as in the case of a solid body a certain amount of air is necessary to ensure complete combustion, so also is it in the case of gases and vapours. Hence, if the necessary amount of (atmospheric) oxygen in the flask be entirely displaced by gasoline vapour, ignition is merely accompanied by simple combustion, occurring at the mouth of the flask only, and regulated by the amount of oxygen coming in contact with the vapour there. If, on the other hand, the air is not entirely displaced, the oxygen remaining inside the flask enables the combustion to proceed more briskly, with slight detonation; and, finally, when sufficient oxygen is left in the flask to ensure the complete combustion of the vapour from 10 drops of gasoline (third experiment), then, owing to the aforesaid miscibility of gases and vapours, the combustion ensues suddenly and takes the character of an explosion accompanied by a report.

On still further reducing the quantity of gasoline to 4 or 5 drops, it will be found that no explosion takes place, but merely a faint detonation, the gasoline vapour in this case being too strongly diluted with air.

It is thus evident that gases and vapours in general are not actually explosive except when mixed with air or oxygen, and then only when the mixture is in definite proportions. Combustible gases and vapours cannot furnish an explosion on ignition, unless the air with which they are mixed contains just sufficient oxygen—neither less nor more—for the complete combustion of the vapour present; and this quantity differs for each gas or vapour. Regarded from this point of view, the explosive gases and vapours lose a good deal of their dangerous repute, since it is but rarely that, in practice, the ratio of mixture of gas and oxygen will exactly coincide with the explosive limit; and, in fact, it is owing to this circumstance that the industrial world is spared countless explosions.

The conditions would be far more dangerous in practical life if we had to deal with pure oxygen instead of air (containing only about 20 per cent. of that gas). Seeing that, even when diluted with 80 per cent. of nitrogen, it is able to cause numerous and powerful explosions, how much more would this be the case if the gas were pure? In an atmosphere of pure oxygen, not only would even very small quantities of any inflammable gas or vapour be liable to explode in a most violent manner, but also very small amounts of the air (as consisting solely of oxygen) would suffice to render explosive pure gases and vapours that would otherwise be merely inflammable and combustible.

For this reason a high explosion risk attaches to establishments where inflammable gases or vapours are disengaged in the ordinary course of operations, and where, in addition, carriers of oxygen (*q.v.*) are used (*i.e.* substances that readily give off large quantities of oxygen).

The mixing of oxygen or air in definite proportion to combustible gases or vapours is not the sole means of inducing explosion in the latter, since they may become explosive when particles of dust are floating about in the gases themselves or in the air. For particulars of these highly dangerous explosions, see *Dust Explosions*.

In respect of explosion risk, solid or liquid explosive substances are more destructive in their action than such as are in the form of gas or vapour.

Previous to the explosion, the solid and liquid explosives occupy merely a comparatively small space; but, on exploding, the hitherto strongly compressed gases and vapours therein suddenly expand and then occupy a volume often many hundred times in excess of the original bulk; hence their destructive power of expansion is very considerable. Gaseous or vaporous explosives, on the other hand, do not expand so largely in volume, since they originally occupied a large space, and are incapable of filling a much greater one.

From the foregoing it will be evident that the air, or the oxygen thereof, plays the chief part in the explosion of gases and vapours; one might, therefore, prefer to ascribe the faculty of explosiveness rather to the air than to the said gases or vapours, and to refer to it as explosive when mixed with such and such a quantity of gas; nevertheless, since neither the air nor its contained oxygen is combustible, whereas the gases or vapours are so, the latter, and not the air, must be considered as the "medium" of the explosion.

In the presence of sufficient oxygen the explosion of a gas or vapour proceeds in the following manner:—

Every chemical reaction, even the smallest, is accompanied by the liberation of heat; as the chemical reaction progresses it is followed by an increase in the amount of heat, which in turn helps to accelerate the reaction; and thus the two advance together, both in highly intimate connection and mutually helpful, until the entire mass of the substance has been heated and chemically converted.

When a burning substance, a match for instance, is placed in contact with the extreme outer limit of an explosive mixture of gas and air, the flame of that substance produces ignition at the point of contact, *i.e.* incites chemical reaction. This reaction, combustion, proceeds superficially from the outside of the mixture towards the centre, and thereby forms a plane of combustion which divides the gaseous mixture into two parts; on the one side are the highly heated products of combustion, and on the other is the still unconsumed gas. The dimensions of the two parts vary in proportion as the plane of combustion moves from the consumed to the unconsumed portion.

The velocity at which this plane advances is different for each gaseous mixture, and depends both on the composition of the mixture and on the pressure to which it is subjected: the higher the velocity the greater the rise in temperature, and this latter in turn directly influences the expansion of the gas and the products of combustion, which thereby exert such a strong pressure on their environment (air, walls, &c.), that

the opposing medium (the containing vessel, &c.) is ruptured, overturned, or burst.

This velocity of propagation of the plane of combustion through explosive mixtures of gas is often extremely rapid, and is comparable to an instantaneous vibration should it occur in a space surrounded by walls but open at the top or on one side; the phenomenon may produce a vacuum there, in consequence of which, and of the action of the external atmospheric pressure on the walls, the latter collapse inwards, towards the site of the explosion, instead of being thrown down in an outward direction.

If such a remarkable occurrence should be observed in a case of fire caused by an explosion, or on the occasion of an explosion or fire alone, it may be taken to indicate the presence of some highly explosive substance, most probably an explosive gas or vapour, the character of which must then be investigated.

Explosions of gas or vapour also occur in rooms or places where, though they may be occupied by explosive gases or vapours, there is neither fire, light, nor other burning substances. Such explosions appear paradoxical, though really capable of ready explanation by the *migration* of the gas or vapour, which, by its relatively higher or lower density in comparison with air, is able to flow from one place to another. The heavier or the lighter a gas or vapour, the greater its tendency to migration; of the former class the only examples that need be cited here are the vapours of ether, benzol, and carbon disulphide, the densities of which are 2.56, 2.77, and 2.64 respectively. Since the density of air is taken as unity, these three vapours are more than two and a-half times heavier than the latter.

In consequence of this high density the individual molecules of the vapours adhere more closely together, and are only with difficulty miscible with or soluble in air. These vapours are given off from the surface of their respective liquids, and tend to sink downwards, thus behaving in a manner exactly opposite to the gases carbon monoxide, coal gas, hydrogen, &c., which, on being liberated into the air, quickly ascend, owing to their specific lightness, and at the same time readily mix with or diffuse through the air itself.

Where readily volatile substances, yielding heavy vapours, are being dealt with in any apartment, the evolved gases or vapours tend to sink by their own weight to a lower level. If the room be on the first or second floor, for instance, the vapours find their way through any cracks or other defects in the floor, and eventually into the room below, or, if the door be left open and there is no great draught, the vapours make their way down the stairs, a continuous stratum of vapour being formed.

The path taken by this wandering stream of vapour is determined by the air currents on the floor, which currents are easily set up in factories by fireplaces, the strong draught of a boiler fire for instance. On encountering such a current of air, the stream of heavy vapour will follow the same course, and should this lead, say, to the boiler or fire, it will be ignited there. This ignition will at first be of a non-explosive character, because the vapour is pure and not mixed with sufficient air to be explosive; the flame will then flash back along the stream of vapour until it reaches the source. Here it encounters an explosive mixture of vapour and air, which it ignites and explodes. Such instances of fire or explosion are said to be produced by remote fire, or **flashing back**; for

their occurrence it is not at all necessary that the source of ignition should be a large boiler fire, since the same effect may be produced by contact with a lighted stove, a lamp, a discarded lighted or burning match, or the like.

Vapours traversing a defective floor may be ignited by the lamp in the room below, or by the stove or lights in an adjoining room, to which they have gained access through the doorway; consequently, in all cases where such streams of vapour are able to be formed and can find an exit, it is necessary that all accessible rooms, above, below, or adjoining, must be properly isolated if they contain any open lights or fires.

Experiments have shown that a strong draught from a boiler or other fire may attract wandering streams of vapour or clouds of gas within a range of ten yards; so that plant or rooms in which substances disengaging such vapours are being treated must be situated at least fifteen yards away from any fireplace or naked light with which they may be in direct communication.

Gases and vapours may be ignited or exploded by heat as well as by flame; in such event, however, the temperature must be comparatively high to produce the effects in question. A list of these explosion temperatures is given below:—

	Degrees C.		Degrees C.
Oxyhydrogen gas . . . . .	620-700	Carbon disulphide vapour . . . . .	100-170
„ under pressure . . . . .	518-606	Acetylene . . . . .	509-515
Carbon monoxide . . . . .	636-814	Propane . . . . .	545-548
Methane . . . . .	656-678	Propylene . . . . .	497-511
Ethane . . . . .	605-622	Coal gas . . . . .	647-649
Ethylene . . . . .	577-599	Hydrogen . . . . .	555

At these temperatures even pure gases and vapours will explode without air; and prolonged exposure to glowing metals, such as iron at 850° C. and platinum, will also produce explosion in the case of most gases. From the above table it is evident that the explosion temperatures for gases and vapours are far higher than the corresponding temperatures for solid and liquid explosives, which, as a glance at their composition will reveal (see *Explosives*), explode as low as 137°-300° C.

As already mentioned, a certain minimum quantity of oxygen (air) is necessary to produce an explosion of any gas or vapour by simple contact with flame. This amount differs in every case; and, moreover, the minimum can be exceeded within certain limits up to a maximum, beyond which the mixture again becomes inexplosive.

The range between the minimum and maximum limits differs for each gas and vapour; if small the explosive range is narrow, and *vice versa*. Gases and vapours exhibiting a narrow range of explosibility are far less dangerous than such as have a wide range, owing to the increased margin of possibilities of explosion existing in the latter case.

A particularly antithetical behaviour in this respect is exhibited by acetylene and coal gas respectively. Mixtures of these gases and air become explosive and inexplosive when the percentages of gas in the mixture attain the following limits:—

	Explosive at	Inexplosive at
Coal gas . . . . .	8 per cent.	23 per cent. and over.
Acetylene . . . . .	3 per cent.	82 per cent. and over.

Hence a mixture of coal gas and air is explosive between the limits of 8 and 23 per cent. of coal gas, below and above which limits the gas merely ignites without explosion; on the other hand, a mixture of acetylene and air is explosive when the proportion of acetylene is as low as 3 per cent., and remains so till it reaches 82 per cent. Acetylene has a wide range of explosibility, coal gas a narrow one; the explosion risk of the latter is low, that of the former very high. The explosibility of explosive mixtures of gas and air may, however, be removed by the presence of carbon dioxide.

The range of explosibility in an admittedly very imperfect series of gases and vapours is given below, the figures in the first column representing the minimum percentage of gas, and those in the second the maximum percentage, at which an explosion of the mixture is possible. The gases are arranged in reverse order, starting with the one exhibiting the highest minimum; and the values cited are merely approximate, great divergence prevailing in the figures given by different authors.

	Percentage.	Approximate Relative Range of Explosibility.
Carbon monoxide . . . . .	13-75	3
Carburetted air (air gas) . . . . .	9-26	5
Water gas . . . . .	9-55	4
Coal gas . . . . .	8-23	6
Hydrogen . . . . .	7-75	2
Carbon disulphide vapour, from 6 downwards }		Merely approximate.
Ether " " 6 " }		
Methane (marsh gas) . . . . .	5-13·16	8
Ethylene . . . . .	4-22	7
Acetylene . . . . .	3-82	1
Benzol (Benzine, 2·6-4·8) . . . . .	3-6	9
Toluol . . . . .	...	about 7
Pentane . . . . .	2·5-5	10

From the above figures it is evident that, in the case of acetylene, hydrogen, and carbon monoxide, the limits of explosibility are very far apart, so that they exhibit a wide range, viz. 3-82, 7-75, and 13-75 per cent. respectively, within which their mixtures are susceptible of explosion.

According to Professor Bunte of Carlsruhe, the limits of explosibility can be greatly varied by circumstances, such as the lateral dimensions of the containing vessel, the method of ignition, volume of gas present, moisture content of same, &c. The same authority gives the following values in the case of electrical ignition, the mixtures of air with the several gases mentioned exploding when the proportion of gas attains the following percentages:—

	Per Cent.	Range of Explosibility.
Carbon monoxide . . . . .	16·6-74·8	58·2
Hydrogen . . . . .	9·5-66·5	57·0
Water gas . . . . .	12·5-66·6	54·1
Acetylene . . . . .	3·2-52·2	49·0
Coal gas . . . . .	8·0-19·0	11·0
Ethylene . . . . .	4·2-14·5	10·3

	Per Cent.	Range of Explosibility.
Alcohol vapour . . . . .	4.0-13.6	9.6
Methane . . . . .	6.2-12.7	6.5
Ether vapour . . . . .	2.9- 7.5	4.6
Benzol vapour . . . . .	2.7- 6.3	3.6
Pentane . . . . .	2.5- 4.8	2.3
Benzine vapour . . . . .	2.5- 4.8	2.3

Above and below these limits no explosion occurs, the mixture merely flashing at the upper limit. The explosion of the mixtures can be prevented by additions of  $7\frac{1}{2}$ -10 per cent. of carbon dioxide.

The reason why acetylene is far more dangerous than hydrogen, and the latter in turn than carbon monoxide, is that mixtures of the first-named with air become explosive when the proportion of gas is as low as 3 per cent., whilst in the others the initial proportion is 7 and 13 per cent. respectively; so that with carbon monoxide four times, and with hydrogen three times, as much of the gas must escape into the air of a room to render its atmosphere explosive, as is the case with acetylene.

With regard to the compression of liquids into gases, enough has already been said under *Temperature*; exposure to pressure increases the fire and explosion risk of all gases and vapours, and may raise them to the same category as blasting explosives. In view of the (sometimes very considerable) dangers then incurred in the production, handling, and carriage of these compressed gases, special legislative enactments have been devised, which need not be particularised here.

The liquefied gases in most extensive use at present are oxygen, hydrogen, carbonic acid, sulphurous acid, ammonia, acetylene, air, and sulphuretted hydrogen.

Nearly all large laboratories and industrial establishments engaged in the manufacture of chemical and pharmaceutical preparations employ these gases in the liquid form, on account of its great convenience and the guarantee it affords, up to a certain point, of chemical purity.

Liquid carbonic acid has made headway in many branches of industry; but unfortunately the best means of installing the steel cylinders are not always adopted. In reference to this matter, the following points may be stated with reference to the fitting up of the gas cylinders and their pipe connections:—

(1) Liquid gases should never be used or stored, not to say manufactured, in workrooms containing inflammable materials or explodable vessels.

(2) The cylinders and pipes may only be placed in suitable cool situations, shaded from the sun and remote from any source of heat (a stove or lamp).

(3) The waste gas that cannot be used again must not be allowed to escape in or towards any place where it might become ignited by sparks, fire, or incandescent material (flues). Exceptions to this rule are afforded by the unflammable gases sulphuric acid, ammonia, and carbon dioxide; but oxygen, though itself unflammable, may stimulate combustion in other burning materials, and should therefore be kept at a distance from fires of all kinds.

(4) The cylinders must fulfil legislative requirements, be officially certified and tested, mounted on secure foundations, provided with safety-

valves of sufficiently strong construction, and have been thoroughly annealed at the time of manufacture.

(5) If the outlet valve be opened very quickly, the temperature in the pressure regulator is raised to a point sufficient to carbonise wood shavings, *i.e.* 160°–200° C. This temperature has been observed in the case of carbon dioxide, which is harmless so far as inflammability is concerned; and in the case of inflammable gases the very rapid opening of the valve would lead to considerable risk of explosion.

(6) Explosions of liquefied combustible gases may easily cause fires, whereas, in the case of incombustible gases, *e.g.* carbon dioxide, ammonia, sulphur dioxide, such a result can only occur when particularly inflammable materials, carriers of oxygen, or dust-yielding substances are present.

(7) With certain gases the escape from the cylinder is accompanied by electrical phenomena, which may prove a source of danger, especially in the case of readily inflammable gases.

(8) Cylinders containing liquid gases should never be heated to more than 30° C., and this temperature, which may readily be attained in the sun, may induce explosion even in the case of the best-made cylinders. Conveying gas cylinders on open waggons, exposed to the heat of the sun, is a dangerous proceeding.

The best method of preventing fire and explosion risks from gases in any establishment is by effecting the timely removal of the dangerous gas or vapour from the workrooms as quickly as possible, or *at once*, by an efficient system of ventilation. Unfortunately, owing to ignorance of the nature of the gases, entirely wrong means are frequently adopted, and most preposterous methods of ventilation installed at great expense.

There is no royal method of ventilation suitable to all cases and all gases, and consequently the means adopted to remove dangerous gases must be in accordance with the nature of the gas in question, its density in particular.

It is not the place here to discourse on the technology of ventilation; it will be sufficient to state that the ventilation of a room containing dangerous gases can be effected either from the level of the ceiling or that of the floor, and is not necessarily confined to the former.

The majority of gases and vapours now under consideration are heavier than air, and will therefore tend to sink down to the floor. In such case it would be fundamentally erroneous to attempt to use a ventilating appliance working at a higher level, and floor ventilation then becomes a *sine quâ non*. On the other hand, ventilation at the ceiling is applicable in the case of specifically lighter gases and vapours.

The only circumstances under which an affirmative answer can be returned to the question whether a powerful ventilator, driven by steam or electricity, in the roof will suffice to remove heavy gases or vapours from a room, in a manner to preclude risk of explosion, are when the room is not large, and in particular not *high*, and the ventilator is sufficiently powerful to produce a constant appreciable draught, which, however, renders the room uninhabitable. For heavy vapours a small ventilator of the simplest kind on the floor will be far more efficient than a powerful ventilator in the roof. With light gases the conditions are naturally reversed, a feeble ventilator in the roof being superior to a stronger one at the floor level.

The greatest difficulty encountered in the removal of gases is when

their density approximates to that of the air, *i.e.* is about 0.9 to 1.1; in such event the best results are obtained by setting up a powerful fan (power-driven, if necessary) in such a position that it can act direct on the place where the gas or vapour is formed, and carry it straight away. Hence, the fan must act directly over open pans, fireplaces, tables, &c., according to the circumstances of each case, and must resemble the appliances now so effectually used in many factories for removing injurious kinds of dust (polishing powder, wood dust, cement dust, lime dust, &c.).

When it is a question of several gases or vapours liable to become mixed in the same room, still further care is necessary in ensuring their immediate removal by a perfect system of ventilation, since such mixed gases are far more dangerous in point of explosibility than if pure. In such cases the ventilation must be arranged in accordance with the density of the gas, &c., produced in largest quantity, and not with the density of the mixed gases.

To facilitate solution of the general problem respecting the comparative advantages of roof and floor ventilation, lists of the gases (*g*) and vapours (*v*) respectively lighter and heavier than air are given below, the density of air being taken as unity.

(1) *Lighter than Air* (Roof Ventilation).

0.069 Hydrogen ( <i>g</i> )	0.700 Wood gas ( <i>g</i> )
0.400–0.600 Coal gas ( <i>g</i> )	0.898 Acetylene ( <i>g</i> )
0.553 Pit gas (Firedamp) ( <i>g</i> )	0.945 Hydrocyanic acid ( <i>g</i> )
0.588 Ammonia ( <i>g</i> )	0.967 Ethylene ( <i>g</i> )
0.622 Water vapour ( <i>v</i> )	0.967 Carbon monoxide ( <i>g</i> )

Water gas, generator gas, Dowson gas, power gas, and similar gases differ considerably in density according to their composition, but are all lighter than air.

0.987–1.015 Mond gas (according to the coal used)

0.510 Water gas

0.830–1.000 Generator gas

(2) *Heavier than Air* (Floor Ventilation).

1.036 Ethane ( <i>g</i> )	1.800 Cyanogen ( <i>g</i> )
1.039 Nitric oxide ( <i>g</i> )	1.935 Butylene ( <i>g</i> )
1.105 Oxygen ( <i>g</i> )	2.004 Butane ( <i>g</i> )
1.120 Methyl alcohol ( <i>v</i> )	2.104 Carbon oxysulphide ( <i>g</i> )
1.185 Phosphuretted hydrogen ( <i>g</i> )	2.200 Sulphur ( <i>v</i> )
1.192 Sulphuretted hydrogen ( <i>g</i> )	2.448 Chlorine ( <i>g</i> )
Air gas (carburetted air) ( <i>v</i> ):—	2.565 Ether ( <i>v</i> )
1.260 With 10% of hydririne	2.645 Carbon disulphide ( <i>v</i> )
1.275 " 11½% " "	2.697 Arseniuretted hydrogen ( <i>v</i> )
1.317 " 14% " "	2.770 Benzol ( <i>v</i> )
1.382 Allylene ( <i>g</i> )	2.784 Seleniuretted hydrogen ( <i>g</i> )
1.451 Propylene ( <i>g</i> )	3.147 Amyl alcohol ( <i>v</i> )
1.520 Propane ( <i>g</i> )	4.215 Chloroform ( <i>v</i> )
1.527 Nitrous oxide ( <i>g</i> )	4.355 Phosphorus ( <i>v</i> )
1.530 Ethyl aldehyde ( <i>v</i> )	4.498 Telluretted hydrogen ( <i>g</i> )
1.590 Hyponitrous acid ( <i>g</i> )	5.700 Selenium ( <i>v</i> )
1.613 Alcohol ( <i>v</i> )	6.650 Sulphur vapour
1.617 Methyl ether ( <i>g</i> )	8.896 Tellurium ( <i>v</i> )
1.738 Methyl chloride ( <i>g</i> )	

## 8. Explosions of Blasting Materials ("Explosives")

Blasting materials, or, as they are generally termed, "Explosives," are explosive substances manufactured in a form convenient for handling, which, on account of their chemical constitution, can only have their accumulated chemical energy released and brought into play by certain means: either by percussion, heating, or detonation, and only at the pleasure of the person by whom they are used. They constitute explosive substances which, as it were, have been tamed to a certain extent; and since they explode only under certain definite conditions, and not under all circumstances, the danger attending the use of explosives compounded according to chemico-technical rules is far less than in the case of other so-called wild explosives (chemical substances like azoimide, nitrogen chloride, chlorates, picrates, &c.), which mostly go off at random and are less powerful in their effects. The explosion risk is lessened:—

(1) By *handliness*; the explosive must be compact and easily handled; consequently, gases, vapours, and liquids are unsuitable, since the storage vessels might break and the contents be spilled, or the gases volatilise.

(2) By *insusceptibility* to the effects of fall, vibration, slight shock, and warming up to 100° C. Certain explosives must be even able to stand direct contact with flame, a condition attained by the addition of inert substances or water. An adjunct of this kind is camphor, of which from  $\frac{1}{2}$ –10 per cent. is used, the amount being increased to as much as 30 per cent. when great insusceptibility is required (see *Celluloid Nitroglycerin*).

(3) By *stability*; the necessary composition being, therefore, such that the chemical and physical characteristics are unaltered by storage, transport, fluctuations of climate, or moisture.

(4) By the possession of an **explosive force commensurate** with the purpose in view, which force, according to the material employed, is either developed slowly—the gases and vapours behaving like elastic substances—or rapidly, like the so-called high-explosives, whereby the gases and vapours behave like solid bodies.

(5) By *uninflammability*: the term "safety explosives" is applied to such as can be set off in a space laden with explosive gases or vapours without causing these latter to explode. These special explosives, *e.g.* Wetterdynamite (firedamp dynamite), Securite, develop when exploded a temperature not exceeding 2200° C. (about 1 kilo. of mass); Kohlen-carbonite disengaging 1821°–1868° C., Roburite 1616° C.; whilst blasting gelatine furnishes 3200° C., Guhrdynamite 2900° C., and guncotton 2650° C. The last three named are not flameproof, and therefore cannot be used in coal mines on account of the firedamp there.

The degree of safety, however, is limited, and, by reason of the special inherent characteristics of explosives, never affords an unconditional, absolute guarantee of security. For this reason different safety limits of temperature are prescribed in various countries; the maximum permitted temperature in Germany, for instance, being 1800°–2000° C., whilst in France no explosive generating a higher temperature than 1500° C. may be used in coal mines, and for quarry work the maximum is 1900° C.

In addition to the explosion temperature, blasting materials generate in exploding a certain heat of compression, owing to the fact that in

closed boreholes they exert a pressure of 6000–10,000 atmospheres; mercury fulminate is said to produce a pressure of 27,000 atmospheres, nitroglycerin 10,000, and nitrocellulose 12,000 atmos.

The temperatures at which blasting materials explode differ considerably, but are in general lower than for the explosive gases:—

In order to explode	Must be heated to
Kieselguhr, with 50 per cent. of nitroglycerin	180°–230° C.
Cellulose dynamite . . . . .	169°–230° C.
Guncotton, compressed . . . . .	186°–201° C.
„ air-dry . . . . .	137°–139° C.
Collodion wool, air-dry . . . . .	186°–199° C.
Celluloid . . . . .	195° C.
Nitroglycerin . . . . .	257° C.
Dynamite . . . . .	197°–200° C.
Blasting gelatine . . . . .	203°–209° C.
Blasting gelatine with camphor . . . . .	174°–182° C.
Mercury fulminate . . . . .	175°–187° C.
Gunpowder . . . . .	270°–300° C.
Picric acid . . . . .	300° C.

The higher figures relate more to heat rapidly applied, the explosion ensuing at the lower temperatures when the heating proceeds more gradually. The reason for this resides in the chemical changes effected in the explosives by slower, and therefore more prolonged, heating, which changes are accomplished and enable explosion to take place at lower temperatures.

Explosives are usually ignited by means of mercury fulminate (detonating caps), which, by the high temperature engendered by detonation, brings them to explode.

The storage, use, transport, &c., of explosives are controlled by plenty of legislative enactments, to which the reader is referred. All that now need be stated is that, wherever blasting materials or explosives of any kind are used, the employment of any sharp, hard instruments or tools should be prohibited; that all shock, hammering, friction, and any mixing of the materials with sharp-edged hard substances, even though in the finest possible state of comminution, must be avoided; metallic alloys, also, cannot be used; and that when any softening or thawing has to be done, only indirect warmth, as of steam or hot water, is admissible, not direct fire or glowing bodies.

## 9. Nitration, and the Explosion of Nitro-compounds

To facilitate comprehension of blasting materials (or at least most of them) and explosives generally, mention must here be made of nitration and nitro-compounds, all of which latter are more or less explosive.

Strictly speaking, a distinction must be drawn between nitro-compounds and nitrates (the salts of nitric acid), because they are chemically different. Owing, however, to the risk of confusion arising from this separation of the two classes, and the consequent increase in the difficulties lying in the path of non-chemists, without any commensurate practical advantage, we will regard the nitrates as being

nitro-compounds, this course being the more justifiable since many nitrates are classed with nitro-compounds in chemical circles and factories.

If organic substances containing **cellulose**—*e.g.* wood, straw, paper, vegetable fibres, hemp, flax, cotton, nettle fibre, jute; flours such as starch; sugars; or organic compounds like benzol, toluol, phenol, glycerin, naphthalene, &c.—be treated with nitric acid, with mixtures of nitric and sulphuric acids, or with mixtures of saltpetre and sulphuric acid, the nitric acid exerts an oxidising action on the substances in question, and “nitrates” them. The general course of the reaction is as follows:—

- |                                 |  |  |
|---------------------------------|--|--|
| (1) Nitric acid furnishes . . . | $\left. \begin{array}{c} \text{Oxygen} \\ + \\ \text{Hydrogen} \end{array} \right\}$             | the residue being termed a “nitro-group.”                              |
| (2) Organic substances furnish  |  | the residue combining with the nitro-group to form a “nitro-compound.” |
|                                 | $\left. \begin{array}{c} \text{the two} \\ \text{forming} \\ \text{Water.} \end{array} \right\}$ |  |

In other words, the nitric acid freed from a portion of its oxygen combines with the organic substance, freed from a portion of its hydrogen, to form a nitro-compound.

According to the strength of the nitric acid, or mixture of which it forms part, and the method employed, different amounts of oxygen and hydrogen are eliminated from the acid and organic matter respectively, and consequently a divergent number of nitro-groups are formed. If these groups are 1, 2, 3, 4, 5, &c., in number, we obtain mononitro-, dinitro-, trinitro-, tetranitro-, pentanitro-, or hexanitro-compounds. For example, trinitrophenol is phenol into which three nitro-groups have entered by nitration (*i.e.* picric acid). Nitration is effected in a number of different ways, the nitrating liquid being added slowly to the substance under treatment in vessels of cast iron, lead, glass, or acid-proof stoneware, which must be cooled with water on account of the high temperature evolved by the reaction; other substances again are directly immersed in the nitric acid.

In order to obtain definite nitro-products it is necessary to exactly regulate the temperature, the supply of the nitrating liquid, and also the time of the reaction, the safety and success of the operation depending on the fulfilment of these conditions. Carelessness may lead to great overheating, spontaneous ignition, and to violent explosion of the whole.

The following list of the chief nitro-compounds with which we are concerned must be regarded as merely typical of the innumerable substances of this class:—

#### A. From the **Nitration of Cellulose substances** (“Nitrocelluloses”).

##### I. From *Cotton* :

1. Dinicrocellulose Collodion wool (Colloxylin). This furnishes—
  - (a) when treated with sulphurous acid = Collodion.
  - (b) dissolved in ether = Collodion.
  - (c) do., but inspissated = Celloidin.
  - (d) treated with camphor = Celluloid.
2. Trinitrocellulose . . . Guncotton (Pyroxylin).

1 and 2 furnish Pyrocollodion, a mixture of di- and trinitrocellulose.

- |                              |                                    |
|------------------------------|------------------------------------|
| II. From <i>Wood</i> . . .   | Wood nitrocellulose, Nitrolignose. |
| III. From <i>Straw</i> . . . | Straw nitrocellulose.              |
| IV. From <i>Jute</i> . . .   | Nitrojute.                         |
| V. From <i>Paper</i> . . .   | Nitropaper.                        |
| VI. From <i>Starch</i> . . . | Nitrostarch, Xyloidin.             |

**B. From the Nitration of Hydrocarbons, Saccharine substances, and the like.**

- |                                  |  |
|----------------------------------|--|
| I. From <i>Benzol</i> (benzene): |  |
| 1. Mononitrobenzol . . .         | Artificial oil of bitter almonds, Oil of mirbane.        |
| 2. Dinitrobenzol.                |  |
| 3. Trinitrobenzol.               |  |
| II. From <i>Toluol</i> . . .     | Trinitrotoluol.  |
| III. From <i>Phenol</i> . . .    | Trinitrophenol, picric acid.                             |
| IV. From <i>Erythrite</i> . . .  | Nitroerythrite, nitric erythrite ether.                  |
| V. From <i>Glycerin</i> . . .    | Nitroglycerin.   |
|                                  | (a) mixed with kieselguhr = dynamite.                    |
|                                  | (b) with collodion wool and camphor = Blasting gelatine. |
| VI. From <i>Sugar</i> . . .      | Nitrosaccharose, Vixorite.                               |
| VII. From <i>Mannite</i> . . .   | Nitromannite, detonating mannite.                        |
| VIII. From <i>Molasses</i> . . . | Nitromolasses.   |
| IX. From <i>Gum</i> . . .        | Nitrogum.  |

Nitration is practised in many chemical works, and the *modus operandi* should be stated, since the fire risk is increased when the nitration exceeds certain limits. It is particularly desirable to ascertain what substances are nitrated, and what amounts are treated per diem.

This is particularly justifiable in taking over insurances, inasmuch as the ordinary schedule of stores, which may be comparatively or entirely harmless of themselves, gives no information as to whether they are employed for nitrating. Thus, no one considers the storing of starch, sugar, glycerin, &c., and of sulphuric acid, nitric acid, and saltpetre, as particularly dangerous; but if the same be used for nitrating, the risk is considerably higher.

A further reason for putting the question about nitration is afforded by the circumstance that the nitration products (nitro-compounds including nitric esters, nitrocelluloses) are mostly recovered merely as intermediate products, which are immediately worked up into innocuous final products. Hence in many cases the preparation of these nitro-products is of a merely transitory character; and it is of importance in estimating the fire risk of an establishment to know whether the operation of nitration is actually practised, no matter whether the dangerous products are stored as such or converted into harmless ones.

If the preparation, though only transitory, of dangerous nitro-products is ascertained, information must be obtained respecting the further treatment, storage, and use of same; for, though all nitro-products are not dangerous, sodium nitroprussiate, nitrocarbon, nitrochloroform, nitrobromoform, nitrotartaric acid, and other substances

often, but erroneously, included among nitro-products, being perfectly harmless, nevertheless the majority are risky, many of them exceedingly so, and necessitate extreme care in handling; it is therefore highly desirable to know what is done with them and how they are treated.

As a rule, the larger the number of nitro-groups in a compound the greater the danger; hence the penta-, tetra-, and trinitro-compounds are generally more dangerous than the di- and mono-compounds.

Provided the nitro-compounds be *chemically pure*, spontaneous ignition and explosion need scarcely be dreaded, if at all. On the other hand, the impurity arising from defective manufacture or imperfect purification often imparts to these products a very high risk of explosion, the worst feature being that such danger rarely becomes manifest at or immediately after the time of manufacture, but usually after some time has elapsed and the goods have been stored.

Impurities destroy the stability of the nitro-products, and spontaneous decomposition sets in, resulting in most serious explosions.

The dangers of the **nitration process** (as distinguished from the products) increase in proportion with the inflammability of the substances to be treated; in the case of cellulose, glycerin, cotton or straw, the risk is far less than when substances like benzol, toluol, or naphthalene, readily inflammable *per se*, are nitrated.

These dangers are most imminent in the manufacture of nitrobenzol (aniline manufacture), spontaneous ignition and explosion not infrequently occurring when the nitrating liquid has been overlooked in the pipes leading to the nitrating vessel, and benzol or toluol is allowed to run through the same pipes; the sudden mixing of the two liquids leads to violent explosions.

The same result may ensue when the nitrating liquid is run into the vessel already charged with benzol before the stirrers have been set to work, or when they are started too late. In such event the mixing of the two substances in large quantities disengages such an amount of heat that the benzol or its vapour may become ignited, an explosion immediately ensuing.

Unsought-for nitration occurs also when acid carboys (*q.v.*) burst or leak in presence of organic substances.

Nitration on a large scale should only be performed in ground floor rooms that are fireproof, isolated, cool, and not exposed to the heat of the sun. The flooring should slope to a collector, and, if of an organic nature (boards or spars), must be kept constantly damp; any sawdust on the floor must also be wetted, and removed in good time when soaked with droppings of the nitrating liquid.

The nitration cloths used in many works are highly dangerous, and even liable to spontaneous ignition if not washed out thoroughly, or when warmed too much in drying; they should be protected from flame or sparks.

No readily inflammable or explosive substances should be stored or treated in nitration chambers, and no other operations should be carried on there. If the arrangements are good and the substances nitrated do not give off any inflammable or explosive vapours, open fires and lights may be permitted, provided they are far enough away from the nitrating vessels, so that they do not directly communicate heat to the latter. Still, even in this case, steam heating and enclosed lights are preferable.

Insurance companies should require that the materials used are as pure as possible, that the greatest care is exercised in eliminating acid from the nitro-products, and that a sufficient supply of cooling and washing water (for removing the acid) is available, since the slightest trace of residual nitric acid in the products greatly increases the risk of explosion. Carrying the products of nitration from place to place in the works should be reduced to a minimum, and exposing the same to pressure during transport or movement must be avoided. The removal of acid by pressing, washing, or centrifugalising should be entrusted to none but skilled workmen, and chemical control must be exercised to ensure the complete elimination of the acid. The use of metal utensils, metal spoons for baling the nitrating liquid, should be prohibited; explosions are liable to occur, and can only be obviated by using wooden or rubber-coated utensils.

To simplify the operation the work of nitrating, eliminating acid, washing and drying is performed in a single vessel, a centrifugal machine. This combination possesses many advantages, and obviates certain dangers present in the ordinary process; but it brings other dangers in its train by enabling larger quantities to be nitrated at a time.

The centrifugal machines have a capacity of 22–44 gallons of nitrating liquid, in which 15–17 lbs. of raw material can be nitrated; and since nitrating occupies about an hour, and the centrifugalising ten minutes, as much as 170 lbs. of raw material can be treated per diem, an accumulation that must be characterised as highly objectionable in the case of such explosive substances. Moreover, centrifugalising is a highly dangerous operation, on account of the risk of sparking and the violent concussion in old or defective machines.

The only permissible method of handling acid carboys is that described under *Carboy Explosions*. In large nitration works the store of nitric acid or ready prepared nitrating liquid (a mixture of nitric and sulphuric acids) is often very considerable. Great care must be bestowed on the waste acid from the nitrating process, since it often contains small quantities of nitro-products, which may cause great damage. For this reason, and because these substances possess a certain value, they are filled into denitrifactors (lead cylinders, lined with acid-proof bricks), and exposed to air and water vapour, thus recovering the valuable nitric acid. In nitroglycerin works in particular, the sludge (containing nitroglycerin) is a special source of danger in winter in the frozen state, which it assumes at 8° C. (see *Nitroglycerin*).

## 10. Explosions of Various Explosive Substances

(a) **Nitroglycerin** (Pyro-glycerin, glyceryl trinitrate, nitrotriglyceride, Nobel's blasting oil, trinitrin, nitroleum, glonoine).

Sp. gr. 1·600, boiling point 185° C., burning point 200°–218° C.; explodes at 257° C., the temperature thereby rising to 6980° C. It is prepared by running glycerin into nitro-sulphuric acid, which must be well cooled on account of the considerable heat evolved; the temperature should not be allowed to exceed 30° C.

On pouring the nitrated mixture into cold water the nitroglycerin

separates out as a yellow oil, which is then freed from acid by the aid of soda. The first batch of soda lye used must be too weak to decompose the nitro-compound, such decomposition being attended with the liberation of so much heat that the other nitro-compounds may be exploded.

The spontaneous decomposition readily occurring in this process betrays itself in advance by the liberation of yellowish-red fumes, and often results in spontaneous explosions (see under *Nitration*); the more impure the product, the greater the danger.

Pure, acid-free nitroglycerin is not attended with such a high explosion risk as is generally believed, but is stable. (The very first sample ever prepared, in 1847, is still preserved, in an unaltered condition, in Nobel's laboratory at Avigliana. Portions of it are tested every year, and are still unchanged.)

If slowly warmed, it may be raised to boiling; but explosion (very violent, it is true) only occurs during strong ebullition.

It explodes with violence under concussion or a blow, but most of all when ignited by mercury fulminate.

In contact with flame it ignites with difficulty, and burns without exploding; in presence of incandescent bodies it behaves in a similar manner; and when poured on to glowing iron it ignites, also without exploding; but if the iron is only warm enough to raise the temperature of the nitroglycerin to  $185^{\circ}$ – $240^{\circ}$  C., then it explodes, since it immediately boils, and in this condition is explosive.

Solutions of nitroglycerin, *e.g.* in methyl alcohol, are far more susceptible to concussion than the pure substance; when exposed to frequent changes of temperature its susceptibility to heat is increased, and when repeatedly warmed and re-cooled it will decompose at as low as  $30^{\circ}$  C., whereas otherwise incipient decomposition does not ensue below  $70^{\circ}$  C.

In the warm it behaves as follows:—

At  $100^{\circ}$  C. it vaporises with difficulty.

$185^{\circ}$  C. boils.

$194^{\circ}$ – $200^{\circ}$  C. volatilises.

$241^{\circ}$  C. detonates.

$257^{\circ}$  C. explodes with great violence.

$267^{\circ}$  C. „ faintly.

$287^{\circ}$  C. „ very faintly, with production of flame.

One gram of nitroglycerin furnishes on exploding 467 c.c. of gas; 1 litre, 750 litres of gas; ordinary gunpowder furnishes only 280.

Nitroglycerin sets at  $8^{\circ}$  C., and is then far more dangerous than in the liquid condition, inasmuch as the hard crystals become strongly heated by mutual friction. Frozen nitroglycerin may be thawed by a temperature of  $11^{\circ}$  C., the operation necessitating great care.

To diminish the high risk of explosion in handling, storage, and transport, and at the same time enable its powerful explosive power to be utilised industrially, nitroglycerin is mixed with kieselguhr (the undecomposed scales of diatoms, diatomaceous earth) to form solid earth. This diatomaceous earth has a high power of absorption in respect of nitroglycerin, 100 parts taking up as much as 75 parts; this proportion, however, must not be exceeded, otherwise the subsequent spontaneous oozing out of the nitroglycerin may be expected, whereby a high explosion risk is imparted to the dynamite.

Since the process of mixing and pressing the two substances can only be effected by friction and pressure, it is a very dangerous operation and attended with violent explosions. On the other hand, the finished product, solid dynamite, which does not exude any nitroglycerin in course of time, is not susceptible to shock, fall, and friction, but can be stored, and may even be held in a flame, burning without explosion when not tightly packed.

Very violent concussion, such as that of a rifle-bullet, will cause it to explode, as also will embedded mercury fulminate ignited by an electric spark.

Unlike nitroglycerin, dynamite must not be exposed to cold; it freezes at  $4^{\circ}$ – $8^{\circ}$  below zero C. To thaw it out again nothing may be used but moist warm sand, which must not be heated above the point at which it still remains damp. Frozen dynamite must not be brought in contact with flame, any glowing substance, or sparks.

In the case of discoveries of explosive materials, &c., designed for felonious purposes, it was at one time a frequent practice to cool them down immediately with ice; but where nitroglycerin or dynamite is in question, this treatment only renders them more dangerous.

(b) **Guncotton** (Pyroxylin, Cellulose hexanitrate, Trinitrocellulose). Ignition point  $160^{\circ}$  C., explosion point  $137^{\circ}$ – $139^{\circ}$  C. when air-dry,  $186^{\circ}$ – $201^{\circ}$  C. when pressed. One gram furnishes 600 c.c. of gas when burned, 755 c.c. when exploded.

Guncotton is readily ignited by the smallest flame, and burns with detonation. It is prepared in the same way as nitroglycerin, but from cotton instead of from glycerin. Chemical purity, and especially freedom from acid, forms the best preventive against the often spontaneous explosions to which this product is liable. \*Above all, care must be taken to use the purest cotton and acid in its preparation.

After expressing the superfluous acid the cotton must be left standing for twenty-four hours, after which it is centrifugalised, freed from acid by means of soda, passed through a breaker, washed, dried, and packed, the moisture content being 25 per cent. So long as the nitrated cotton remains moist the method is not attended with any great dangers, these first arising in the pressing and drying.

A stronger acid and somewhat higher temperature are employed for guncotton than for collodion wool; the latter is soluble in ether, the other not. Guncotton is more highly nitrated, and contains more nitro-groups, being therefore more dangerous than collodion wool; these form the main differences between the two products.

In estimating the extent of the risk a distinction must be drawn between wet and dry guncotton.

*Wet* guncotton can be controlled by mechanical means. It does not explode by the action of flame, glowing carbon, or metal, by shock or blows; but, on the other hand, is highly explosive under the influence of ignited mercury fulminate, even when submerged in water. It is also exploded by dynamite, nitroglycerin, and *dry* guncotton.

*Dry* guncotton is exceedingly inflammable, but is not very susceptible to shock or friction when in a compressed state, though when stored it is liable to decompose spontaneously, great danger then arising from the formation of cellulose derivatives of a spontaneously explosive character.

This danger, which may also arise in the purest guncotton, is said to be preventible by washing the guncotton with dilute acetone.

Guncotton exerts its maximum explosive power when packed in tightly closed packages.

Both kinds of guncotton must be stored in perfectly fire-proof places, which must be kept cool, the stability of the product being destroyed by exposure to temperatures of 30° C. and over. Moreover, the period of storage must not be unduly prolonged. The packing must be good, and the degree of compression low, since all pressure increases the risk, and also the tendency to spontaneous decomposition. Under prolonged storage, even the merest traces of acid are very dangerous. Storage in a partial vacuum is no protection against spontaneous decomposition, but rather favourable thereto.

Conflagrations of loose or lightly packed guncotton are not invariably attended with explosion of the rest; but if it is contained in tightly closed metal packages, and these are exposed to the heat of the fire for some time, an explosion is easily possible.

Guncotton (and also collodion wool, to an equal extent) is used in the manufacture of numerous preparations, chiefly explosives; it furnishes with—

- |                                      |   |
|--------------------------------------|---|
| (1) Nitroglycerin . . . .            | Blasting gelatine, Nobel's powder.      |
| (2) Picrates . . . .                 | Melinite.                               |
| (3) Glacial acetic acid . . .        | Scale powder.                           |
| (4) Nitronaphthalene and Nitrobenzol | Plastomenite (also serving as varnish). |

*Blasting gelatine*, although composed of two highly explosive substances, nitroglycerin (90 per cent.) and guncotton, or collodion wool (10 per cent.), is less dangerous than dynamite, because it usually also contains a little camphor. It burns like dynamite, and when heated to 270° C. flames up like gunpowder. Also in the frozen state it is less dangerous than dynamite or nitroglycerin, but is more susceptible to concussion than when in the soft, unfrozen condition.

Under water it explodes with violence, and in closed vessels it explodes at 203°–209° C.

(c) **Collodion wool** (Colloxylin, Cellulose tetranitrate, Photoxylinum). Ignition point 150°–160° C.; explodes at 186°–199° C.

This substance is very similar to guncotton (*q.v.* for the preparation). Although far less explosive than guncotton, it must be very carefully handled, especially in the dry state. Its conveyance by rail or post is prohibited, owing to its often very capricious behaviour. The danger is diminished by the presence of at least 15 per cent. of moisture, and a similar effect is produced by dissolving it in alcoholic solutions of certain salts, such as calcium chloride, magnesium chloride, zinc chloride, potassium acetate or ammonium acetate.

Collodion wool forms the raw material for numerous preparations, which are never devoid of danger, even though, in part, they do not stand on the same high plane, in this respect, as the material itself. Thus it furnishes—

When treated with sulphurous acid, *Colloidin*, used for photographic purposes.

When dissolved in ether, *Collodion*, for medical and surgical purposes.

When swollen by the addition of a very small quantity of ether, *Celloidin* (concentrated collodion).

When mixed with camphor, *Celluloid* (*q.v.*).

With nitroglycerin, *Blasting gelatine*, for blasting.

With amyl acetate, *Zapon lacquer* (see *Varnish*).

With regard to these several substances, in so far as they are not specially dealt with, the following remarks may be made:—

Colloidin behaves exactly like collodion wool itself, but is in a more highly purified condition; it is a source of danger in photographic studios.

Collodion is about on the same level as ether in point of inflammability and liability to explosion; its employment is attended with the evolution of no small quantity of ethereal vapours (see *Ether*). That it is not a more frequent source of accidents is due to the circumstance that it is mostly used in small quantities, must be kept tightly stoppered in order to remain good, and is usually employed only by skilled users (doctors, chemists, and photographers). Under friction, the dry residue left on the evaporation of the ether becomes highly electrified, up to sparking point; it is therefore dangerous to treat dried collodion with ether or benzol again, since the vapours of these substances may be ignited by electric sparks.

Celloidin is far less dangerous than collodion (like which it behaves in other respects), since it liberates little or no ethereal vapour. (For *Celluloid*, *Blasting gelatine*, and *Zapon lacquer*, see separate headings.)

Collodion, collodion, and celloidin are all largely used in works for the manufacture of photographic papers, transfer pictures, transparencies, so-called collodion pictures, &c.; and all these trades are very dangerous in point of fire and explosion risks, on account of the great quantities of ether-, acetic ether-, and spirit-vapours evolved. Special danger attaches to the rooms where the evaporation of the ether, &c., is effected (drying rooms), owing to the possibility of the production of electric sparks in the ethereal atmosphere.

(*d*) **Celluloid** (erroneously also termed hard rubber, artificial rubber) is camphorated nitrocellulose. It decomposes at 140° C., being at the same time readily inflammable, and explodes at 195° C. The celluloid first manufactured was termed xylonite or Parkesite, and was very dangerous.

It is a so-called pyroxylin mass (guncotton), which is impregnated with camphor, pressed and rolled.

There are very few substances known over whose fire risk such fundamentally divergent views have obtained, and still prevail, as the interesting material cellulose. At one time it is characterised as highly explosive, at another as quite harmless; sometimes it has proved explosive in practice, and at others exhibited an entirely innocuous behaviour. For a long time the character of celluloid was problematical, because both views were found justified, some commercial articles of this material being highly dangerous, whilst others proved perfectly harmless.

At present celluloid may be said to be not very explosive, though readily inflammable; and if it formerly had a different reputation, the sole reason must be sought in the fundamentally divergent composition and method of preparation. Celluloid must be admitted as extremely inflammable, but it only becomes explosive under well-defined conditions. It might therefore have been dealt with in another place; but, being

prepared from an explosive substance, and exhibiting numerous analogies with the nitrocellulose preparations, we may proceed with its properties, &c., now as follows.

The great tendency to explosion exhibited by guncotton or collodion wool is diminished by an addition of camphor, the product in either case being celluloid, which in turn only manifests a disposition to explode when struck against a hard object, to the point of sparking, or when heated above  $195^{\circ}\text{C}$ .

At  $140^{\circ}\text{C}$ . it decomposes and flashes, the same result ensuing when it is placed in contact with flame or incandescent bodies; but in neither event is an explosion produced. This latter eventuality is only possible when the burning celluloid gives off inflammable vapours in large quantity, a condition that may easily arise on an outbreak of fire occurring in a large store of celluloid.

Although a good testimonial may be given to celluloid in respect of explosion risk, it must not, on the other hand, be concealed that many celluloid articles in popular use have proved so highly inflammable (defective manufacture, insufficient camphor), that a certain mistrust of this substance would seem justified. Fortunately, however, this applies solely to badly washed, impure celluloid, which, it is true, may be caused to detonate by very gentle heat (the sun's rays), the radiant heat of a stove, a lamp, or even an electric incandescent lamp. A comb made of such material was caused to detonate (a phenomenon bordering on spontaneous ignition) by the friction to which it was subjected in a lady's pocket.

Celluloid, and of course also all articles made from this substance, is readily inflammable from its large percentage of oxygen, sufficient indeed to support the combustion without any adventitious supply of air. Celluloid fires are therefore very difficult to extinguish, no assistance being afforded by excluding air, even by the aid of steam; nor is water of any use. In this respect, celluloid resembles carriers of oxygen (*g.v.*), and is therefore highly explosive when held in suspension, in the state of fine dust, in the air. A cloud of such celluloid dust may easily form about the machines wherein this substance is being worked, and the same may become very dangerous in the vicinity of open lights or fire, unless the dust is immediately removed by an efficient system of ventilation.

All celluloid articles, whether in store (in shops) or in use, must be kept at a distance of at least 20 inches from any source of heat, and must, in particular, be sheltered from warm draughts, the rays of the sun, and from radiant heat; this applies specially to articles in shops and shop windows.

Celluloid is prepared by treating guncotton or collodion wool with melted camphor, or camphor dissolved in ether and alcohol. The mass is kneaded warm, an operation rendered dangerous by the evolution of ether-alcohol vapour; and the only way to obviate this risk is by good ventilation and the removal of all fires and open lights to a distance. Still greater danger is incurred in the pressing, and the final warming of the mass to  $100^{\circ}\text{C}$ ., to eliminate the last traces of alcohol and enclosed air-bubbles. The manufacture is therefore attended with numerous risks. The operation of dyeing celluloid is also very dangerous, by reason of the inflammable solvents employed (acetone, acetic ether, alcohol, ethyl acetate).

In the same manner as the explosibility of celluloid (or rather, gun-cotton and collodion wool) can be nullified by camphor, it was thought possible to diminish its inflammability by additions of such salts as magnesium chloride, aluminium sulphate, sodium silicate, phosphatic compounds, zinc chloride, lead borate, &c. The attempts, however, proved unsuccessful, and it would seem that inflammability is a permanent and irremediable property of celluloid. Some slight amelioration in this respect is effected by the use of camphor substitutes, like naphthyl acetate, acetochlorhydrine, acetine (the acetic ether of glycerin). Nitronaphthalene is also employed for this purpose, but with doubtful results. On the other hand, all these substances often entail the use of dangerous solvents, like benzol, collodion, ether, &c., which increase the danger of manufacture. In insurances, these substances should be specified individually.

Celluloid is now substituted everywhere for rubber, glass, metal, horn, amber, &c.; even bandages (*q.v.*) are impregnated with celluloid solution (comp. *Acetone*), and thus rendered inflammable. Celluloid pictures, artificial amber, varnishes, Zapon lacquer, are all made of celluloid; and all these articles, when stored in shop windows, or wherever exposed to strong sunlight, or open lights (especially gas), or where sparking may occur, constitute a by no means insignificant source of danger, which is the greater in proportion as the articles themselves are finer and more delicate, the flame spreading more rapidly the more easily combustion is effected. Consequently also, accumulations of pulverulent and fragmentary celluloid waste are specially dangerous directly they are exposed to contact with even the smallest open flame or spark. Celluloid is often employed for waterproofing textiles, and also as a leather substitute (Pegamoid, Dermatoid); and is itself replaced by Gallalite, prepared from curd (casein).

All rooms wherein celluloid is prepared, used, or stored must be fire-proof in every direction; and special attention must be devoted to celluloid waste and the storing of same.

(e) **Other Nitro-compounds.**—The nitration of other substances, such as straw, wood, jute, paper, starch and sugar is of less importance, industrially, than that of cotton, because these substances are more difficult to obtain pure, and therefore furnish impure products possessing an extremely high explosion risk, owing to their liability to spontaneous ignition. Most of these nitro-compounds can only be exploded by mercury fulminate, but ignite on contact with flame and burn away quietly in the air. In closed vessels they are explosive, like guncotton, though inferior to the latter in explosive force.

If wood that is to be nitrated is still resinous, the resulting nitrocellulose products are doubly dangerous; hence only wood free from resin should be used.

To increase the stability of nitrocellulose it is boiled, and washed with alternately hot and cold water, in pans under a pressure of three atmospheres. The pressure, which is attended with a temperature of 135° C., increases the danger of the process.

Of these nitrocelluloses, only the following need brief mention—

*Xyloidin* (nitrostarch) ignites on contact with flame, and at 170°–178° C.; another, more highly nitrated, starch ignites at 155° C., and both are exploded by a blow.

*Nitrojute* ignites on contact with flame and at 162°–170° C., and burns quietly. Under a powerful blow it explodes.

*Nitropaper*, see *Paper*.

*Nitrostraw* (straw nitrocellulose) is almost impossible to obtain in a pure state, owing to the difficulties in the way of purification. Consequently it is very liable to spontaneous decomposition, and also to explode arbitrarily, a temperature of 170° C. being sufficient to produce explosion.

*Nitrosaccharose* (nitrosugar, vixorite) explodes when struck.

*Nitromannite* (mannite nitric ether) detonates at 120° C., and explodes when struck. It readily decomposes during storage, and may then lead to spontaneous explosions. When properly used, carefully prepared, and suitably mixed, it constitutes one of the most powerful explosives known; but, when impure, is one of the most dangerous.

*Nitromolasses*, from the nitration of molasses, explodes at 220°–250° C.

*Nitrogum* is but little known and seldom met with.

Certain hydrocarbons, such as benzol, toluol and their compounds, are also easily nitrated, the dangers of the operation being, however, augmented by the formation and ignition of explosive vapours, especially in the case of benzol.

(f) **Nitrobenzol**.—There are several varieties of nitrobenzol, oil of mirbane being one. As finished products they are far less dangerous than any other nitro-compounds, and are only now mentioned on account of the danger arising, in the manufacturing process, from the ignition and explosion of the benzol as a result of spontaneous heating. This risk may be obviated by powerful cooling. Again, in distilling these products explosions may result from the overheating of the still walls. When nitrobenzol is treated with soda lye, alcohol, and zinc dust, **benzidine** (diamidodiphenyl) is obtained. On account of the considerable degree of spontaneous heating this process is very dangerous, and special precautions must be adopted in adding the zinc dust, or a very violent reaction will ensue. To prevent the violent explosions occurring in this process (which in one case, at Crefeld, caused a loss of five lives) the apparatus must be fitted with a wide flue, leading into the outer air and closed by a very thin sheet of lead, which bursts as soon as a heavy pressure is developed. The benzidine itself is harmless.

Nitrobenzols are largely used in aniline manufacture. There are three commercial grades—

	Sp. gr.	B. p.
Light . . . . .	1.200	205°–210° C.
Heavy . . . . .	1.190	210°–220° C.
Extra heavy . . . . .	1.167	222°–225° C.

(The terms light, heavy, &c., refer to the boiling point and not to the density.)

(g) **Nitrotoluol**.—Of the various nitrotoluols, boiling from 230° to 300° C., we need mention only *trinitrotoluol*, boiling at 300° C. This is not very susceptible to the influence of flame, friction, or percussion; when poured on to glowing metal it burns away quietly, but when exposed to prolonged heating it decomposes finally with flaming detonation. Heated in closed vessels it explodes violently, and is therefore largely used in the manufacture of blasting materials, a

very powerful explosive being produced by mixing it with ammonium nitrate.

(h) **Nitroerythrite**.—This, the nitric ether of erythrite, is prepared by nitrating the latter substance, and is highly explosive under percussion, but merely detonates when heated in the air.

(i) **Picric Acid** (trinitrophenol) is an important product, obtained by the nitration of phenol (carbolic acid), and one deserving more ample consideration.

Picric acid is also known as trinitrocarbolic acid, picrinitric acid, carbonitric acid, and Welter's bitters. It fuses at 122° C., flashes at 150° C., and explodes at 300° C. The acid forms pale yellow scales, which become deep yellow when picrates are present (see below).

In the pure, scaly condition, and free from extraneous substances, picric acid has a low fire and explosive risk, will stand gradual warming up to 150° C., also friction, percussion, and shock, provided they are not too violent. In contact with a naked light it burns, but detonates when warmed quickly, and explodes when heated rapidly to 300° C.

Should any part of the picric acid detonate, this, especially if repeated, may cause the whole to explode. Similarly, an explosion of picric acid may be caused by violent shock or friction, contact with falling burning masses, and (though with difficulty) by the electric spark.

All these dangers can be considerably lessened by converting the picric acid from the scaly form—

1. By careful fusion or pressing (antithetical to guncotton, which becomes more explosive when compressed);
2. By making it into a paste with gum arabic, fat, or oil;
3. By dissolving it in water;
4. By mixing it with a 3–5 per cent. jelly of collodion in ether-alcohol.

The least dangerous forms of picric acid are the fused and pasty conditions, though Nos. 3 and 4 are almost harmless; and indeed very violent external influences are required to cause explosion in any one of these four states.

On the other hand, the risk of explosion may become extremely high—

5. If the acid be combined with a base to form a salt, a picrate, *e.g.* potassium picrate;

6. If it is not thoroughly freed from by-products at the time of preparation, as happens in the case of many other nitro-compounds;

7. If it be adulterated by the addition of picrates, common salt, saltpetre, alum, Glauber salt, sugar, borax, oxalic acid, &c.;

8. Or mixed with carriers of oxygen, such as manganese peroxide, potassium chromate, spirit of turpentine, ozone, hydrogen peroxide, &c.;

9. When the acid is brought into contact with a burning substance that generates a considerable amount of heat during combustion; in such event the combustion at once becomes explosive. Pure, fine picric acid is able, in burning, to absorb its own heat of combustion, but if the latter be supplemented by an extraneous source of more intense heat, such, for instance, as glowing metal, coal, the oxyhydrogen flame, &c., then the still unconsumed picric acid will explode. Hence picric acid may be considered as presenting risk of explosion only when its combustion is supported by another burning substance giving out great heat.

10. If heated—though merely to the fusing point—when tightly packed in closed vessels.

Under certain circumstances, therefore, picric acid is an almost harmless body for insurance purposes, whilst under other conditions it may become a dangerous source of explosion; on the other hand, its salts, and the impure or adulterated acid itself, as also when exposed to the conditions (5–10) set forth above, should not be accepted as insurance risks. The great picric acid explosion at Griesheim (25th April 1901) is attributed to the machinery having become heated in running.

When unaccompanied by the formation of picrates, the manufacture of picric acid is not a particularly dangerous process, no inflammable vapours being given off by carbolic acid during nitration. The carbolic acid is added to the nitric acid drop by drop, and the whole warmed for one or two hours. The picric acid then crystallises out and is dried, an operation free from danger if performed in suitable apparatus and with careful attention. Of course the temperature must be under proper control. Unfortunately, it is sometimes necessary, especially when chemically pure picric acid is required, that picrates must first be formed, from which, when purified, the acid is precipitated. The explosion risk of the picrates is diminished by the circumstance of their being in a state of solution or submersion throughout the process; and the real danger only sets in when they are dried, a course that is not always necessary. Small quantities of these salts may, with very great caution, be dried at temperatures up to 70°–80° C., the early stages being performed at relatively low temperatures, which must be raised very gradually.

For insurance companies it becomes highly important to know whether *salts of picric acid* are made, and if they are immediately decomposed for the production of picric acid, or dried as commercial articles and stored. In the latter contingency, no insurance should be granted.

Wherever large quantities of picric acid are stored a proper system of lightning conductors must be provided.

Picric acid is not very largely used in the pure, dry state, though very often employed in the less dangerous condition of a solution, or paste moistened with glycerin, by the dyer, in bandages for burns, and for impregnating sawdust to eliminate naphthalene from coal gas. In the latter event it is not impossible that the danger may be increased by the formation of picric salts, *e.g.* of ammonia. The products thus formed are still too little known for anything to be said about them, except that care is advisable. The picrates are almost exclusively used in the manufacture of explosives, *e.g.* melinite and lyddite shells.

By the action of ammonium sulphide on picric acid, salts of picraminic acid are formed, and these are explosive if heated rapidly. Lead picrate, one of the most dangerous salts of the picrate series, is used in the silk industry; it renders the fabric liable to spontaneous ignition.

Picric acid ends the list of the chief explosive nitro-compounds, and we now come to a series of explosive substances of an altogether different character.

(k) **Diazobenzol** forms, with acids, compounds of an extremely explosive nature.

Diazobenzol chromate (aniline fulminate) is on a par with mercury fulminate, and is exceedingly dangerous in every respect.

Diazobenzol nitrate, when struck or heated, explodes even more violently than mercury fulminate.

Diazobenzol chloride also explodes under similar conditions, but less powerfully than the foregoing.

Diazobenzol sulphate explodes when struck, and also when heated to 100° C.

Notwithstanding their violence, explosions of the diazobenzols are flameless, and on this account they have been proposed for blasting in inflammable atmospheres (fiery mines).

In the case of diazobenzolsulphonic acid great care must be exercised when it has been kept for several years; old samples of this kind have exploded merely on being handled with a porcelain spoon.

(l) **Ammonium nitrate** takes fire when gently warmed with acetic acid, but is only explosive (and then very violently so) when used in association with nitro-compounds, *e.g.* nitronaphthalene. The analogous *ammonium nitrite* explodes when struck or when heated to 70° C.

(m) **Chlorates**.—These powerfully explosive compounds act by liberating oxygen (see *Carriers of Oxygen*). They are more dangerous than the nitrates, and, under some conditions, also than the picrates.

The chief chlorates are those of potassium and lead. They explode with great violence when ground, pounded, or warmed along with organic substances (sugar, flour, powdered fruits, spices, wood), or with carbon, phosphorus, sulphur, or powdered metals. Still more powerful explosions may be produced in association with potassium cyanide or thiocyanate, sulphides (iron or antimony sulphide), matches, or firework charges. On account of certain susceptible characteristics of chlorates the works where they are produced have a very high explosion risk, and are greatly endangered by the proximity of other plant wherein sulphuretted hydrogen is liberated. Should this gas find its way into the chlorate works it readily acts on the metal of machinery and apparatus to produce metallic sulphides, which get mixed with the chlorate and explode on the slightest provocation. Hence no works disengaging sulphuretted hydrogen, or treating metallic sulphides, should be tolerated in the vicinity of a chlorate factory.

Chlorate works are just as susceptible towards fats and oils, these readily allowing the chlorate to explode; and, unless the most stringent precautions be taken to prevent oil or greasy rags, &c., being conveyed in any way to the chlorate plant from the engine or boiler-house, or from the room where the lamps are filled, cleaned, &c., a most violent explosion may be produced at any time, probably attended with the entire destruction of the works. As a means of precaution, oil lamps should be banished from chlorate works, and all greasy rags, &c., burned at once.

If, for any purposes (*e.g.* the preparation of oxygen), the chlorate is warmed in closed vessels, it has a great tendency to choke up the gas outlet, whereupon the growing pressure of the liberated gas may burst the vessel and cause the chlorate to explode, even far below its true explosion temperature. The violence of such explosion is the greater because of the presence of the liberated oxygen. In fusing chlorate the temperature must not exceed 360° C., at which point the liberation of

oxygen and increased explosion risk begin. Unlike picric acid, the dangers of chlorate are not lessened by fusion.

Explosions may also be produced in breaking lumps of chlorate that have dried hard; should a few crystals of chlorate remain in the neck of a stoppered bottle and suffer attrition when the stopper is inserted, an explosion may be produced. Soft stoppers (rubber, wood, cork) alone should be used for chlorate bottles, and the rubber must be free from sulphur. Packing paper, millboard, &c., for chlorate must be made fire-proof by impregnation. In the storerooms, &c., all possible precautions must be taken against the spread of fire, and the factory and store must be separated in a fire-proof manner. All articles that might absorb chlorate (*e.g.* wood, articles of clothing, rags, wrapping paper, &c.) must either be sent out of the factory, or else washed free from chlorate before being used again; for this reason iron, and not wood, should be used for the apparatus, the coolers especially. Anything likely to produce sparks must be avoided, and all organic materials, even dust, must be protected from the chance of admixture with chlorate, since the latter renders them very inflammable.

Strong acids must be kept from contact with chlorate, or explosive gases like chlorine tetroxide will be formed.

In itself the preparation of potassium chlorate is not a very dangerous operation. At present it is conducted on a large scale by the electrolytic decomposition of potassium chloride; also by passing chlorine gas through milk of lime, the resulting calcium chlorate being decomposed by potassium chloride. The sole dangers, therefore, are those arising from the electric current and the chance of spontaneous heating, the latter, however, being comparatively unobjectionable, since only solutions, and not solid masses, are concerned.

The chief danger first arises in the drying of the finished product, which is effected in centrifugal machines (risk of sparking!), and in grinding the dried mass, an operation requiring the greatest caution.

Wherever chlorates of any kind are used there is always risk, and in particularly dangerous establishments these compounds should, as far as possible, be replaced by others of a safer character, calcium plumbate being applicable in some instances.

Chloric acid is the explosive constituent in all chlorates, and this acid when prepared in a concentrated state is capable of producing spontaneous ignition in organic substances like paper, wood, linen, straw, textiles, fibres, and the like, by mere contact and being left to dry thereon. Inquiry should therefore be made in the case of every chlorate factory whether any chloric acid is made.

(n) **Fulminates, Detonators.**—When alcohol is gently warmed along with a nitrate, *e.g.* of gold, silver, or mercury, there results a highly explosive compound termed a fulminate. The acid component is not prepared separately. Gold fulminate is also obtained by adding ammonia to gold chloride. The silver compound is the most violently explosive.

Fulminates are extremely dangerous, being for the most part explosive, even in a moist state or under water; and their preparation, manipulation, and storage are dangerous occupations in the sense of explosive risk.

If water or other liquid with which a fulminate has been mixed is spirted about and the drops left to dry, the slightest residual traces

of the fulminate will explode of themselves; the greatest violence being exhibited when they are exposed to the rays of the sun.

Even the dust swept up in fulminate works has a tendency to explode spontaneously; hence all aqueous, dusty waste products, all lixiviation-rinsing and washing water must be deprived of this tendency by a boiling-off process—which may also be attended with danger, owing to the temperature ( $98^{\circ}\text{C.}$ )—before removal.

Fulminates are largely used in the firework and blasting material industries for the preparation of detonating pellets, detonating charges, caps, and detonators. All these preparations are explosive if exposed to shock, falls, friction, concussion, heat, flame, or acids; and where large amounts are in question, the results may be disastrous. Where fulminate factories are situated near other works, special care must be taken to render all waste innocuous and prevent any being scattered or spilled about. The term fulminate is often applied to substances that are different in composition from the true fulminates, such, for instance, as potassium chlorate, and also a mixture of sulphur, saltpetre, and potash; this latter product can be prepared without danger, but when finished will explode with great violence under very slight heating or by a blow.

Gold fulminate is used, especially in solution, for gilding, and so long as it is in this condition, or suitably moist, it is harmless enough, but in the dry state it explodes at the first opportunity.

Fulminates will rarely stand warming as high as  $100^{\circ}\text{C.}$ , nor will they bear exposure to an electric spark or naked flame.

(o) **Gunpowder.**—In itself gunpowder is less explosive than readily inflammable, detonating; but as under certain conditions (in a confined space) it may also give rise to very violent explosions, it will be briefly dealt with here. It consists mainly of 75 per cent. saltpetre, 10–12 per cent. sulphur, and 12–16 per cent. charcoal; ignites at  $270^{\circ}$ – $300^{\circ}\text{C.}$ , generating a temperature of  $2200^{\circ}$ , and a pressure of about 6000 atmospheres; and the resulting gases occupy about 280 times the volume of the original powder. The danger of gunpowder resides in its extreme inflammability. The only occasions when capricious explosions of this substance occur are when the saltpetre used contains chlorine, the highly auto-explosive compound nitrogen chloride (*g.v.*) being then formed; or again, if the powder be repeatedly heated and re-cooled—hence the residue left in the drying rooms is always liable to spontaneous explosion, and these rooms should, therefore, always be scrupulously cleaned out. The sulphur, also, must be pure, and free from sulphurous acid—*i.e.* in sticks, not flowers of sulphur. The charcoal must be made at a temperature not lower than  $400^{\circ}\text{C.}$  to preclude the possibility of containing readily and spontaneously inflammable constituents. The presence, also, of  $1$ – $2\frac{1}{2}$  per cent. of potassium perchlorate in the saltpetre may induce spontaneous explosion of the powder. If these conditions be fulfilled, there is very little that can be urged against gunpowder beyond its inflammable nature. The manufacture is naturally a risky process, the operations of mixing and drying the materials (at  $50^{\circ}$ – $60^{\circ}$ ) and the compressing of the powder under a pressure of 1700–1800 lbs. all entailing great caution.

The finished product is ignited by any flame, any glowing body or electric spark, and also by being heated to  $270^{\circ}$ – $300^{\circ}\text{C.}$  Again, shock, friction, or percussion can ignite gunpowder, the result being more easily

obtained when the impact or friction is produced by two bodies of the same material, *e.g.* iron against iron, brass against brass, than in the case of iron against brass, or *vice versa*. Tin and tin alloys should be excluded from use in powder factories, owing to the ease with which dangerous tin compounds are formed.

Copper and lead are the two metals which ignite gunpowder with the greatest difficulty. Hard or encrusted masses of powder should not be broken, pounded, scraped or rubbed down in the dry state.

Strangely enough, loose gunpowder is not always ignited by lightning, and the frequency of instances where lightning has been known to strike stores of loose powder without any result seems to justify the conclusion that the air pressure exerted by the flash disperses the powder and drives it out of contact with the actual spark: even if a few grains be ignited they are insufficient to set fire to the dispersing particles. On the other hand, powder that is tightly packed or has become coherent through moisture is easily ignited by lightning.

The presence of an admixture of fat diminishes the inflammability of gunpowder, 2-4 per cent. for fine and 10 per cent. for coarse grained powder, being sufficient to retard the rapidity of combustion as well as reduce the inflammability. When gunpowder is used in theatres, shooting galleries, and other enclosed spaces the wads must be of some material that will consume rapidly and completely, without being able to transmit flame to any other articles. Paper is unsuitable, but cow-hair or the like will do.

Powder can be prevented from exploding on contact with glowing bodies by additions of pulverulent incombustible substances, such as sand or powdered glass, which retard the transmission of the phenomena of explosion through the mass.

(p) **Azoimide** (*Nitrogen hydride*).—Boils at  $+15^{\circ}\text{C.}$ , and is an extremely explosive substance, 0.05 gram being sufficient to produce great devastation. The preparation and handling are exceedingly dangerous, and it will not stand either concussion or heat. The danger may be diminished by dissolving it in water, but unless the solution is very dilute it will burn on contact with flame.

With silver or mercury it forms explosive salts; and those furnished by potash, soda, or lime, though less explosive, must always, as a matter of precaution, be stored under water.

(q) **Explosive Compounds of Nitrogen with Chlorine, Bromine, Iodine, and Sulphur** (*Nitrogen chloride*).—The character and appearance of this substance are expressed by the name it received from its discoverer, "Dulong's explosive oil." The method of preparation is free from danger, chlorine gas being passed through dissolved sal ammoniac; but the product itself is extremely liable to explode on the slightest opportunity, even vibration being sufficient. Owing to its similar behaviour in presence of other substances, it must be kept out of contact with phosphorus and oxygen-free phosphorus compounds, ammonia, arsenic, selenium, potash, soda, fatty and ethereal oils, fats, turpentine, and caoutchouc, both during preparation and storage. Contact with these substances induces immediate explosion, even though the nitrogen chloride be still wet or moist.

When dried, it explodes on exposure to the sun or to artificial light. If the nitrogen chloride be pure the explosion is flameless, but when the

phenomenon results from contact with some inflammable substance, like those mentioned above, this latter takes fire, and a conflagration may ensue.

The other two compounds, *nitrogen bromide* (an explosive oil) and *nitrogen iodide* (an explosive black powder), closely resemble nitrogen chloride in explosive character; even the naturally very damp nitrogen iodide can be exploded by the influence of direct sunlight. Its explosive tendency is so great that when a small quantity is laid on one end of a long bench it goes off if one merely sits down, with the greatest possible care, on the other end. In certain cases the sound waves produced during a concert have been known to cause the explosion of nitrogen chloride and iodide.

*Nitrogen sulphide*, a yellow substance, is far inferior to the foregoing in explosibility, but is nevertheless highly explosive under friction and shock, as also at 179° C. It differs from the others in flaming (sulphur combustion) on explosion, and therefore may have an igniting action.

(*r*) **Liquid Air** (see *Low Temperatures*).—Air (a mixture of about 80 per cent. of nitrogen and 20 per cent. of oxygen) can be liquefied at a pressure of 39 atmos. when cooled to -140° C., and in this condition is a very powerful explosive, the chief part in this connection being played by the oxygen rather than the nitrogen. On being left to evaporate, liquid air liberates a greater proportion of nitrogen, this being the more volatile constituent, whilst the residual liquid, which is enriched in oxygen, becomes more explosive.

This oxygenated air resembles dynamite, can be lighted by a flame, and burns without explosion, but when ignited with a little detonating material gives a very powerful explosion, which can be still further intensified by adding to the air some organic substance, such as cotton, petroleum, or ether. The mixture, however, retains its explosive character for a short time only, this diminishing in a quarter of an hour, and disappearing entirely within a further space of half-an-hour. This peculiarity is of great value in blasting, since it eliminates the dangerous after-explosions otherwise imminent. (See also under *Gases*.)

(*s*) **Dust Explosions**.—In the case of gas explosions an essential condition is the presence of air or oxygen in a certain proportion, the majority of gases and vapours being merely inflammable, and not explosive, in the pure state. A gas or vapour may nevertheless become explosive without the presence of sufficient (or indeed any) air or oxygen should it contain any powdered substance in a state of suspension as fine dust, which latter then partly or wholly takes the place of air or oxygen.

The explosion of such a mixture of gas or vapour with air and dust is termed a dust explosion, an expression we will retain, even though it is not chemically accurate in many instances, the dust merely burning on ignition, and inducing the explosion properly so-called.

The same behaviour as is exhibited by the finely comminuted dust of numerous organic substances is also manifested by the dust of many metals, which in the compact state will only burn with difficulty, if at all, though in a finely divided condition they can be readily induced to ignite.

The chief reason for this ready inflammability of dust is the occlusion of atmospheric oxygen, or other gases or vapours present, by the minute

particles of dust, which act like an absorbent sponge. In the same manner as oily or fatty substances, on penetrating textiles and fibres, are caused to present an extremely large superficial area, whereby they exert on the atmospheric oxygen so great a surface attraction that the oxygen is able to react chemically on the fat itself, so do the highly porous particles of suspended dust absorb gases (especially oxygen) and vapours.

Laden with gas or vapour these dust particles form a highly inflammable material, which ignites with great rapidity, forming an atmosphere of hydrocarbons and carbon monoxide that furnishes with the remaining air an explosive mixture, which is ignited and exploded by the flame of the burning dust.

Consequently, dust explosions occur in two stages: the ignition of the dust particles, and the explosion of the resulting and ready formed gaseous products. These two phases follow in such rapid succession as to practically form one operation.

Pure metallic dust of various kinds (see *Bronze powders*) may also explode without the presence of any other gas besides air.

Both organic and metallic dusts become far more explosive when mixed with substances liberating oxygen, *e.g.* colophony, resins, ozone, peroxides, carriers of oxygen, &c.; in addition to facilitating explosibility these also considerably augment the explosive power; therefore all such substances (see *Carriers of Oxygen*) should be kept away from pulverulent materials.

As a rule, dust explosions are of a violent nature; those of metallic dust less so, unless oxyhydrogen gas is in question (see *Bronze powders*). Dust explosions have been known to occur in the case of the substances mentioned below, when the same have been floating in a finely divided state in the air, and ignited by a flame or spark

Carbon, of almost every kind, except purified wood charcoal;

Lampblack;

Wood dust, cork, tan, decayed wood (see *Wood*);

Grain, bran, malt, cleanings;

Flour, starch, sugar, dextrin;

Wool, fibres, textiles, tow, fluff from shearing;

Metals, bronze powders;

Colophony, resins, celluloid;

Sulphur, naphthalene.

Any kind of dust floating in the air can be ignited by the simplest flame, or by electric or other sparks.

The explosion of dust is considerably facilitated by a preliminary warming, or the introduction of a warm gas. Violent motion of the dust particles will also contribute to their explosion; but, on the other hand, shock, percussion, or friction, unaccompanied by the production of sparks, can never cause dust explosions.

Like explosions of gas and vapour, dust explosions may also be induced by remote fire. Thus, for instance, flour or finely ground substances in the course of bagging, handling, transport, the bursting of a bag or the opening of a bin, &c., may produce clouds of dust, which, making their way through shafts, stairways, &c., may come in contact with a naked light or open fire; on ignition they light back to the starting point, where the ignition terminates in an explosion,

mostly attended with great devastation. Explosions of this kind have been not infrequently observed in flour mills.

The method in which the dust is produced, and the space where this occurs, greatly influence the degree of the resulting danger. Dust, in the form of long-suspended clouds, can be formed :

(1) By the simple *combustion* of the materials, as in the case of lamp black ;

(2) By dry distillation, *sublimation* : sulphur, naphthalene ;

(3) By mechanical *pulverisation* (grinding, pounding, beating) : in powder or flour mills ;

(4) By mechanical *purification* (screening and blowing) : in agricultural machines for grain, malt, &c. ;

(5) In *waste* or the *débris* from goods in bulk : removing the materials from place to place in mills, maltings, &c.

(6) By the *bursting* of bags or other storage appliances, a possible contingency in any business.

The formation of dust is most dangerous in classes 5 and 6, being then sudden and unexpected. The occurrences numbered 3 and 4 are less dangerous, and Nos. 1 and 2 least of all, since under ordinary working conditions the formation of dust proceeds but slowly.

The more rapidly and violently the dust is formed, and the finer the state of division, the greater the possibility of a powerful explosion.

With reference to the question of space or locality, it may be stated that rooms or vessels that are completely enclosed are the safest, provided there is no chance of sparking or ignition. On the other hand, danger attaches to all places where the presence of flues, hoists, lifts, or other imperfectly closed apertures affords opportunities for the escape of the dust externally, and therefore to some light or fireplace. Such fireplaces with powerful draught, boiler fires, furnaces of any kind, are standing sources of danger to rooms where dust is produced.

The formation of dust is always accompanied by a liberation of heat, though this is too insignificant to cause ignition, except when the dust is produced in enclosed vessels and the dissipation of the heat is prevented, in which event the inflammability of the materials determines whether or no the accumulated heat will result in an explosion. Even under favourable conditions, such an eventuality is not altogether precluded ; and it is therefore necessary to provide some method of dissipating the heat, especially where the machinery or apparatus (*e.g.* cleaning machinery) has a tendency to get hot in running, since hot machine parts have often been the cause of dust explosions (*e.g.* the picric acid explosion at Griesheim).

It is difficult to lay down any other general rules for preventing dust explosions, owing to the highly divergent nature of the various kinds of dust, apart from the appliances used.

The heating of machine parts may be detected by painting them with pigments that change colour at high temperatures. For instance, a mixture of mercury iodide and copper iodide, which is red at the ordinary temperature, turns black at 60° C., the red colour reappearing on cooling. In very dusty establishments, where the occurrence of inflammable gases or vapours (*e.g.* coal gas, ether vapour) is not precluded, the following general regulations may be laid down :—

(a) The rooms where dust is produced must be well ventilated, the air being changed three times per hour if possible ;

(b) Dust resulting from the mechanical treatment of any substance (in turning or polishing, for instance) should be drawn away by an exhaust as soon as formed. In the case of light and heavy dust, motor-driven suction appliances must be situated close to the machinery and apparatus producing the dust ;

(c) Where the dust is produced inside any apparatus (cleaning or screening machinery, &c.), the latter must be kept tightly shut, or else completely enclosed in a wooden casing, to prevent any escape of the dust to the outside of the machine ;

(d) Dusty material must be stored in such a manner as to preclude risk of dispersion by falling bodies, the dropping of the material or the bursting of the packages ;

(e) Machinery, &c., in which dust is produced must not be opened until sufficient time has elapsed for the dust to subside after the machinery has ceased running ;

(f) Where the nature of the materials permits, the air must be humidified ; damp air, being lighter, allows the dust to settle down more rapidly ;

(g) Inside lights—except electric glow lamps, fitted with double glass bulbs for greater safety—must be prohibited in all machinery where dust is produced ;

(h) Workrooms where dust is formed must be lighted from the outside by protected lamps only, except where electric glow lamps are used, as under g ;

(i) Workrooms containing any inflammable gas or vapour in addition to dust must not be entered with any other lights than safety-lamps (*q.v.*), so long as the said gases or vapours are known to be present.

The main features of explosions produced by the various kinds of dust will be referred to when dealing with the substances in question. At present only the following points need be mentioned :—

*Cork dust*, which chiefly occurs in cork mills and linoleum works, is of a highly dangerous character (explosion risk), owing to its extreme fineness and capacity for remaining suspended in the air for a long time.

The same applies in no smaller degree to the *dust from wool, cotton*, and other fibres. Cotton furnishes up to 14 per cent. of its weight of dust. The fluff from shearing machines in cloth finishing is specially liable to explode.

*Malt dust*, also, has caused dangerous explosions (the Tottenham Brewery was destroyed in this manner) ; and a large sugar works was annihilated by an explosion of sugar dust, damage to the extent of some £300,000 being done, owing to the removal of the wooden casing of a grinding mill, and to the escaping dust catching fire at an adjacent gas flame.

The most frequent instances of dust explosions on a large scale are afforded by flour, the dust from which is the most liable to explode of any, owing to the various favourable concomitant circumstances.

Sparks are easily produced by allowing the stones to run dry or empty, the machines to get hot, or by the presence of stones or nails in the corn, and all these possibilities favour the ignition of the dust. The

necessary frequent opening of the mills, and the vessels containing dust, leads to explosions when naked lights are in the vicinity; and these explosions may be of a highly disastrous character when several machines, &c., containing dust are in communication.

Clouds of dust, spreading in all directions and filling the entire works, may be produced when large quantities of flour are shot down chutes, or by the falling or bursting of sacks. In such event any small hidden flame may easily ignite the whole explosive cloud of dust.

Dry milling is, in this respect, more dangerous than the wet process. Flour is far more readily inflammable in summer, or even at a temperature of 30° C. (86° F.), than in winter; and it may become almost as inflammable and explosive as lycopodium (*q.v.*).

The explosion of flour is often attributed to the fat present, it being asserted that the natural fat ( $\frac{1}{2}$ – $2\frac{1}{2}$  per cent.) is exposed to the air during milling, and plays the same part as fat or oil in greasy rags does to the fibre. This view, however, cannot be supported, since, were it correct, this fat would cause spontaneous heating (and even ignition) in the mass of the flour. No such instances have yet been observed, at least in such a form that the cause could be traced to the fat present.

On the other hand, it has been noticed that damp flour and other kinds of meal give off hydrogen gas during storage, and even liberate methane in the same manner as other organic matter in a state of incipient putrefaction. The presence of these gases in flour, even when in small proportion, is sufficient to increase the inflammability and explosibility of the article.

The risk of explosion is still further intensified by the affinity for oxygen displayed by damp flour, the gas in question being well adapted to augment the inflammability of the material in presence of hydrogen and methane.

Dust explosions in flour mills, silos, &c., most frequently occur after Sundays and holidays, *i.e.* when the flour has been left undisturbed for some time in closed bins, and then all at once set in motion accompanied by the formation of dust clouds. Possibly, during this period of repose, an accumulation of gas arises in the flour, which gas, when disseminated with the dust, explodes when the flour takes fire on contact with a light or other igniting agent.

Where stored flour or grain is observed to give off a disagreeable odour, which can only arise from hydrocarbon gases, the rooms and bins, &c., must be thoroughly ventilated before the material is set in motion, or any chance is given for clouds of dust to form. As a precautionary measure, all storage chambers should be well and thoroughly ventilated after any short stoppage (on Monday mornings and the day after a holiday).

The great influence exerted on the explosibility of mixtures of gas and air by any floating dust, not merely from flour but from any other substance, organic or purely metallic in character, may be gathered from the following data:—

A mixture of coal gas and air first becomes explosive when the gas amounts to 8 per cent. of the total volume; with

8–12 per cent. of coal gas the mixture burns with a noise.		
12–23	„	„ explodes.

When the mixture contains a little dust from lampblack or flour, audible combustion occurs with 3 per cent. of gas instead of 8 per cent., and actual explosion with 8 per cent. instead of 12 per cent. of gas.

A mixture of coal gas and air, containing 3 per cent. of the former, will not burn at all, unless a little dust be present; and though no explosion need be dreaded in a mixture containing 8–12 per cent. of coal gas, the same will occur in presence of dust; hence coal gas is an objectionable illuminant in grinding mills.

The conditions are analogous in the case of methane, since, whilst the explosive limit of a mixture of this gas and air is not reached until the percentage of gas attains 5 per cent., the presence of a little of any kind of dust renders even a 3 per cent. mixture explosive. And, as already mentioned, methane—even to the necessary extent of 3 per cent.—may be produced in damp flour (see also *Lampblack* and *Coal*).

## CHAPTER V

### FIREPROOFING

WE shall naturally here deal with this question from the chemico-technical standpoint exclusively, and not from that of building authorities or fire insurance companies; but it is impossible to avoid a short discursion into the chemistry of building materials, as well as a statement of the principal requirements that should be fulfilled, both by the works as a whole and by the storages. These remarks apply chiefly to establishments and substances exhibiting a high fire risk, but almost equally so to such as are of a less dangerous character.

The word fireproof is often very improperly used, no distinction being drawn between *fireproof* and *flameproof*. The changes produced in a body by heat are of a twofold character: chemical, inasmuch as the substance burns, and thus sustains alterations both in form and composition; or physical, the form alone being changed, though the strength and solidity in particular suffer, whilst no chemical alteration is produced.

Any substance that remains chemically and physically quite unchanged under the influence of heat is said to be fireproof. This term implies not merely the possession of so-called incombustibility, or chemical stability, but also physical stability: and as most of the substances usually classed as fireproof suffer considerable change of form when exposed to high temperatures, there are very few materials that really merit that appellation: asbestos, magnesite, and alumina. On the other hand, granite, though thoroughly incombustible, cannot be considered fireproof, since it splits like glass even at ordinary fire heat, and granite stairways and arches in a burning house are rendered highly unsafe. Similarly, limestone is by no means fireproof, since it is destroyed chemically (and therefore also physically) even at 600°–800° C.—fire heat often attains 1400°–1500° C.—by parting with its carbon dioxide, the resulting quicklime then slaking to powder in presence of water.

With reference to protection against fire, it is by no means essential that the materials used should be absolutely fireproof, since the possession

of two other properties, namely, *bad conduction of heat*, and *proof against flame*, afford far greater defence against the attacks of fire than the first named.

A substance that is susceptible to the action of heat is best preserved from the destructive influence of fire by wrapping it in some material that is impervious to heat: a bad conductor.

Wood is a poor conductor of heat, but metals—and stone also to some extent—are good conductors. Under certain conditions, wood will afford greater protection to inflammable materials, in the event of fire, than a wall of metal or stone that quickly grows red-hot and thus readily ignites the materials in question.

The usual building materials differ greatly in their behaviour in point of protection against fire and in their conductivity of heat, the ratio in the latter particular being approximately as follows:—

Cement plaster . . . . .	100
Ordinary plaster, stucco . . . . .	112
Oak timber . . . . .	168
Asphalt . . . . .	225
Brick . . . . .	330
Slate . . . . .	500
Cast iron . . . . .	5000

In cases of fire, the smallest amount of heat will be transmitted by a cement wall, this affording the greatest protection; whilst the minimum protection is given by the almost fireproof cast iron, which allows about fifty times as much heat to pass through as cement does.

Oak timber comes very near cement in this respect; but wood is open to the objection that it burns through very quickly, perhaps before the fire is extinguished, and therefore cannot afford any lasting protection. This may apply to ordinary common wood; but it has already been stated that wood is only really protective under certain conditions, namely, when it possesses the additional property of being *flameproof*.

This term is bestowed on substances that burn or transmit flame merely gradually to other substances when exposed to the action of fire. When an otherwise readily inflammable substance, such as a wooden wall, possesses the two properties of low conductivity and proof against flame, it is superior in protective power to others that are far more fireproof in themselves. Exposed to fire, it is acted upon merely in a one-sided and gradual manner; but the main thing is that it protects adjacent materials from the influence of heat, and when employed as pillars or girders it will uphold the roof, without bending or altering its position, *i.e.* it keeps a burning building from collapsing.

From their nature, all organic substances are combustible, being neither fire- nor flameproof. They can, however, be endowed with the latter quality, and then be successfully used as a protection against fire, since, though they char externally, they do not transmit flame, and therefore the latter is prevented from spreading.

The following substances may be rendered flameproof: wood, paper, leather, textiles, fibres, straw, millboard, &c. (for flameproof explosives see under *Explosion of Blasting Materials*).

Latterly, the flameproof materials industry has made great progress; but is still far from a state of perfection, being retarded by the poor

quality of many of the so-called flameproof articles on the market, that when put to the test are anything but what they profess to be. The consequence is that a prejudice has arisen against everything claiming to be fireproof or flameproof; and fire insurance companies have every reason for caution in accepting risks relating to so-called flameproof goods, since it is a very difficult matter to convert articles into a really flameproof condition. The chief difficulty in this connection consists in the fact that no single process is applicable to all classes of goods, but each kind must be treated in a special manner.

A substance or article is fireproof only when it has been rendered un-inflammable throughout its entire mass, and not merely on the surface. The degree of uninflammability increases with the thickness of the stratum that has been made flameproof, and attains its maximum when that stratum extends right through the material. Another point to be insisted on is that the flameproof condition should be permanent, and not diminished or nullified by the action of shock, pressure, heat, changes of temperature, atmospheric conditions, frost, wet, sunshine, wind, time, or by the use, washing, or cleaning of the article treated. This last requirement of permanence is the most difficult to fulfil, whilst at the same time the most important of all.

When the attainment of complete uninflammability throughout is impossible, one has to be contented with securing a perfectly flameproof surface. The means by which such a surface is produced are usually termed "antipyrenes," and mostly consist of chemical salts, or mixtures of same, applied to the article by repeated coatings or dippings, in the state of solution. The resulting uninflammability, however, is only temporary.

According to the extensive experiments of P. Lochtin, with blotting paper, plain paper, cellulose, wood, &c., only twelve antipyrenes were efficacious out of forty-four tested, namely:

Ammonium phosphate, ammonium sulphate, ammonium chloride, calcium chloride, magnesium chloride, zinc chloride, zinc sulphate (white vitriol), stannous chloride, alum, borax, boric acid, and aluminium hydrate.

Of the remaining thirty-two, fifteen proved effective only when applied in large quantity, and were therefore quite unreliable, whilst seventeen actually facilitated the spread of fire.

To the fifteen unreliable antipyrenes belong:

Acetic acid, phosphatic compounds other than the one mentioned above, aluminium borate, zinc borate, tungstic acid and its salts, potash, and silica.

The seventeen substances actually favouring combustion were: sodium sulphite and hyposulphite, carbonates, potassium chloride, common salt, ferrous sulphate (green vitriol), calcium sulphate (gypsum), and sodium silicate (water glass).

The last two groups exhibited the following defects: Cracking off under the influence of heat; imperfect covering of the surface, owing to the crystals failing to melt in the heat of the fire, as they should do, in order to afford protection against flame; imparting brittleness to the objects treated; becoming detached from the surface, on the articles being used, washed, &c. Consequently, the protection afforded by treating articles in common use (wooden objects, curtains, household and body linen, clothing, carpets, &c.) with even the best antipyrenes is merely of

a very temporary character (see under *Wood*). Moreover, even in using the best antipyrenes, chemical considerations must not be disregarded; thus, for chemical reasons, it is inadmissible to use calcium or magnesium chloride as a dressing to render curtains unflammable, since the hygroscopic qualities of these substances will prevent the treated articles from drying at all.

In the case of dyed goods, the use of alum and stannous chloride, which has an acid reaction, or of the alkaline substance, borax, is attended with a destruction of the colour; articles that are exposed to rain cannot be treated with ammonium compounds, or other soluble antipyrenes, for obvious reasons; and, in fact, the only two substances suitable are silica or alumina, both of them very difficult of application.

It is therefore evident that in the attainment of even merely superficial inflammability it is necessary to proceed in accordance with the laws of chemistry; and, in view of the possibility of numerous errors, which may lead to deplorable results, such superficial protection should be regarded with suspicion.

The antipyrenes act in very different ways. The ammonium compounds liberate fire-quenching ammoniacal vapours at  $280^{\circ}$ – $300^{\circ}$  C.; the chlorine compounds act by disengaging vapours of hydrochloric acid, the sulphatic compounds sulphurous vapours, both of which extinguish fire; borax and boric acid form a fireproof coating of boric anhydride; and alumina and silica both act in a similar manner.

So many dangerous cases of fire have occurred in **clothing** that, for certain purposes and in certain works, the fireproofing of garments is advisable and necessary. Workmen engaged in the vicinity of sources of considerable heat (boiler fires, glass furnaces, pottery kilns, foundries, limekilns, &c.) should wear tight-fitting clothes, so that no loose flapping portions may come in contact with the fire. When garments are exposed to protracted heat they become thoroughly desiccated and therefore brittle, in which condition the fabric readily chars and is then ignited by the merest spark.

This danger is greatly increased when the garments become greasy from any cause; in such event the risk of spontaneous ignition is imminent, more especially if the men are working in a dusty atmosphere of any kind whatsoever (from coal, flour, cork, wood, fibres, fabrics, rags, or even metals), such dust, in conjunction with the fat, imparting pyrophorous tendencies to the clothes and rendering them liable to take fire spontaneously.

Cases have indeed been known where such clothes have ignited spontaneously when hanging up undisturbed, and hence it is essential to provide fireproof clothing for workers engaged in establishments where danger is liable to arise from the presence of fat and dust simultaneously. In such event—as indeed with all porous materials—the unflammability, to be of any value, must not solely be confined to the surface of the goods but extend to the core of every individual fibre. True, the expensive process of fireproofing may be dispensed with if the garments be beaten daily and washed at intervals; but it is difficult to ensure this being regularly done.

The sparking or short-circuiting of electric wires, &c., may be a source of danger to clothes, if the latter carry any metallic fittings or trimmings (metallic tinsel on ballet costumes), or are impregnated with

chlorates, nitrates, picrates, or fulminates; special danger in this connection is incurred in breaking electric circuits, starting and stopping electrically driven machinery, &c. The arms, in particular, should be protected by rubber sleeves or mantles.

When flameproof clothing is beaten or washed its safety in this respect is diminished, the antipyrenes used being imperfectly retained by the individual fibres; hence the garments need either to be reimpregnated, or else must be beaten daily and washed at frequent intervals. The garments now under consideration, whether made flameproof or not, should never be hung up near any source of heat, or packed tightly in any confined space (see under *Spontaneous Ignition of Coal-dust*).

It is also possible to make an entire establishment flameproof, at least to a certain degree, by carefully seeing that all and sundry of the materials therein are rendered unflammable. Though this is not practicable in every case, still much may be attained by systematic procedure. Before, however, going into this question, mention may be made of the results of the tests made a few years ago respecting the *fireproof* character of various building materials.

The following materials were exposed to the action of fire, and found to behave exceedingly well:—

(1) Mixtures of cement and crude asbestos, used as insulating material for ironwork, stood temperatures of 1300° C.

(2) Artificial stone steps (G. A. Schütz & Co., Berlin).

(3) Bockler's patent cement boards, for insulating iron girders, iron pillars, wooden beams. No flexion was observed at high temperatures.

(4) Gypsum boards (O. A. Mack), for filling hollow spaces, protective roofing, intermediate boarding, and panelling. Prevent the transmission of heat.

(5) Kleine's pumice slabs proved fairly fireproof.

(6) Monier stairways and arches behaved particularly well under load and at high temperatures.

The following were pronounced *good*:—

(7) Cork brick (of cork, lime, and clay), made by Grünstein & Hartmann, of Ludwigshafen, especially for partitions.

(8) Schubert's (Breslau) plaster for ceilings and walls, also for insulating iron girders.

(9) Mannesmann pillars embedded in cement.

(10) Monier doors, by Hubert & Co., Breslau.

(11) Xylolith (Otto Senig & Co.), particularly for floorings.

(12) Wire roofing glass (Fr. Siemens, Dresden). Though the sheets bent under the weight of heavy falling objects, when in a glowing state, they did not break.

The undermentioned were *not good*:—

(13) Heilmann's isothermal material, the girders bending, and the ceilings breaking up

(14) Magnesite doors and walls bent and cracked.

(15) Granite staircases burst with a loud report, like glass.

(16) Fretzdorff & Co.'s fireproof paint.

It should also be mentioned that neither sandstone nor limestone can be classed as flameproof, not to say fireproof, or is capable of affording any protection whatsoever in case of fire, since the former cracks at red heat, and the latter is converted into quicklime at 600°–800° C.

To make buildings or establishments fire-proof throughout, two courses may be adopted:

(1) By employing none but fireproof and un inflammable building materials, and avoiding all combustible substances—this method reducing the risk of outbreaks of fire to a minimum; or

(2) By adopting precautions to ensure any outbreak of fire being immediately suppressed.

Since, however, it is practically impossible to carry out these two systems separately, the two must be combined, a procedure leading to the establishment of the following general rules for protecting specially dangerous installations against “chemical” fire risks:—

I. Granite, limestone, sandstone, and uncovered ironwork must be avoided in places where great heat may be generated and come into action.

Ironwork (girders, pillars) must invariably be embedded in flame-proof materials (see *Test Fires*).

II. Cavities of any kind in roofs, walls, flooring, &c., must be filled up with un inflammable materials.

III. Doors and windows must be made to open outwards. Where dangerous gases and liquids are produced or used, there must be no communication, by way of doors or windows, with rooms containing open fires, lights, heating apparatus, or anything liable to generate sparks. Electroglass, a transparent, fireproof variety of glass, is suitable for dangerous rooms, shops, show-windows, and stairways.

Doors should be of wood only, covered on both sides with tinplate.

IV. Stairways must be closed in, and constructed of flameproof material.

V. Steam, hot water, or hot air should be the sole means of heating employed. Where stoves are unavoidable, they must be fired from the outside; and the joints must be kept tight, to prevent air entering the stove from the room (see *Stove Explosions*).

The stove pipes must not be placed near any woodwork, and the mouths of the pipes must be covered with a grating (see *Wood*).

VI. The only means of lighting permissible are electric incandescent lamps, with double globes and wire cover, or properly protected outside lights. All taps, switches, &c., for the lamps must be placed outside.

In addition, a number of safety-lamps, in good condition, must be provided for rooms containing dangerous vapours or gases (see *Safety-Lamps*). In the case of less dangerous establishments, petroleum, with a flashing point of not less than 48° C., may be used.

VII. Workmen and others engaged on the premises must not carry any matches or other means of producing a light; consequently, where particularly dangerous gases and vapours are in question, the workmen's clothing should not contain pockets.

VIII. Where dangerous gases and dust are present, efficient ventilation must be maintained, the fans, &c., being driven by motors, and mounted in a manner according with the nature of the gases (see *Gas Explosions*).

IX. Fire-extinguishing appliances must be provided and kept in perfect order (electric fire-alarms, hydrants, fire-cocks, hose, water supply, jets; and the premises must be inspected by watchmen during

the night and on holidays). The extinguishers must be examined from time to time.

X. The steam plant must be isolated from the rest of the premises, and be constructed and worked in accordance with legislative requirements.

XI. All machinery must be mounted in such a manner as to preclude risk of injury (by dangerous fluids) or destruction of the lighting appliances in the event of breakage or explosion of any quick-running machine parts.

XII. All pipes and conduits for the conveyance of steam, gases, hot or dangerous liquids must be enclosed in reliably flameproof material (see *Insulating Materials*), properly protected from the influence of explosions, and kept free from dust—though never so fine—and all fatty or oily substances.

XIII. No machinery, driving belts, or machine parts capable of producing sparks of any kind (electromotors, dynamos, centrifugal machines, driving belts, grinding or polishing wheels, &c.), should be erected or worked in any room where explosive dust is produced, or where gases or vapours are generated or stored in a compressed state.

XIV. Rooms containing dangerous gases or vapours must not be traversed, used as storerooms, or for other operations.

XV. Dangerous gases and vapours must not be allowed to gain uncontrolled access to other rooms, flues, shafts, machinery, or driving belts, but must be confined to the places where they are produced or employed, and only conducted through safe conduits or by means of efficient ventilators to the spots where they can be utilised without danger or discharged without risk of ignition.

XVI. The lubricants used must be suitable for the movement and weight of the machinery lubricated. Any fibrous or other material employed for removing grease must be selected with a view to minimising the risk of spontaneous heating or ignition.

XVII. Waste of any kind must be collected daily, and stored in a suitable way to prevent danger of fire, or be destroyed (oil rags).

Waste gases must be discharged into the open air through pipes; liquid waste caught in suitable vessels; dust and solid waste rendered innocuous by storage in fireproof vessels in a safe place, or consumed.

XVIII. Every manufacturing process that is attended with the production of explosive dust, gases or vapours, the generation of high temperatures, or the utilisation of inflammable or explosive substances, or liquefied gases, must be isolated from all other processes, and, in particular, must not be carried on in the presence of stored goods.

XIX. Notices relating to precautions against accidents, and other instructions to workmen, must be posted in accordance with the regulations.

The precautions to be adopted in storerooms are given below. In this case a far greater degree of safety can be attained than in workrooms, where all manner of contingencies may arise. On the other hand, the dangers incurred in storerooms, even when no work is carried on there, should not be underestimated—they are present, though more easily and effectually combated. Only in one particular is the danger greater in storerooms than in the factory, namely, the possibility of spontaneous ignition, or spontaneous heating, of the goods stored.

By means of proper control, however, this danger, though not invariably precluded entirely, can be readily detected and successfully counteracted.

The fire risks arising in storerooms on dangerous premises, or containing dangerous goods, may be considerably diminished by adopting the following precautions:—

I. In point of construction, heating, lighting, and fire-extinguishing appliances, storerooms must comply with the regulations already prescribed in the case of factories.

II. The floor must invariably be solid, impervious to fluids, and slope gently in one direction, but must not contain any open drain leading to the outside or to other buildings or rooms. A collecting pit must be sunk at the deepest part of the floor, large enough to collect any drainage; and from this pit the drained liquid must be immediately removed.

III. No conduits, gutters, &c., from other rooms, or from outside, should debouch into the storeroom, except ventilating apertures of proper construction and suitably protected.

IV. Windows, or apertures of any kind, must be arranged at a high level, and grated to prevent the access of burning bodies.

V. The means of ventilation must be adapted to the nature of the gases and vapours produced, and these products must not be discharged into any chimney flue.

VI. Storerooms must be protected from lightning, and dangers arising from proximity to railways or other establishments.

VII. All storage vessels must be kept closed, mounted with a free space underneath, and set at such a height that any leakage can be detected immediately. In filling them, space must be left for the expansion of the contents. No vessel should be allowed to drip, but every one that is tapped must be fitted with a drip collector; all collecting, measuring, and filling utensils must be of unbreakable materials, and vessels for filling highly volatile liquids must be of such construction that it is impossible for any flame to light back to the interior while they are being emptied. According to Mack & Grünwald (Dresden), this end is attained by closing the vessel with a perforated stopper, the interior orifice of which is protected by fine wire gauze—a system analogous to that of the safety-lamp. Liquids must be filled solely by the aid of hose pipe, made of some material that is neither corroded nor dissolved by the liquid in question. Carboys and similar receptacles containing dangerous liquids should only be handled by means of suitable tilting appliances of strong construction.

VIII. In the case of goods that cannot or must not be extinguished by water in the event of fire (*e.g.* oils, fats, varnishes, lacquers, resins, mineral oils, tar, benzol, carbon disulphide, &c.) a sufficient stock of sand, fine earth, ashes, or the like, with tools for handling same, must be kept at hand in the storeroom.

IX. Substances liable to heat or ignite spontaneously must not be stored along with strong-smelling articles, the latter tending to prevent detection of the gaseous products liberated by the former during heating, &c.

X. Such goods, when stored loose in bulk, must be kept perfectly level, free from moisture, and not be piled up too thickly. Any wooden

pillars in the centre of the heaps must be impregnated or coated with flameproof materials.

XI. At the entrance to every storeroom, notices must be posted relating to the exclusion of unauthorised persons, smoking, lighting with naked lamps, the carrying of matches, &c.

XII. Storerooms must be kept locked and in charge of a single responsible person, who must be acquainted with the character of the goods stored.

XIII. Stocks of goods or products, whether large or small, in store should be inspected at least once a week; and should any alteration (in the smell especially) be detected, suitable precautions must be adopted.

XIV. Substances of different kinds must not be stored together indiscriminately; but due regard must be paid to their mutual compatibility. For instance, the substances mentioned in the following list may cause outbreaks of fire if stored in contact with one another. For the sake of brevity only one example is given (in the principal list) in the case of groups of similar materials, thus:

*Organic substances* comprise all kinds of coal, peat, flour, starch, sugar, herbs, fruit, seeds, bran, grist, chaff, straw, concentrated fodder, artificial fertilisers (except those of a purely mineral nature), wood, cork, horn, paper, millboard, rags, fibres, textiles, wool, silk, cotton, flax, hemp, and leather.

*Dusty substances*: all pulverulent materials that readily form clouds of dust: like flour, lampblack, bronze powders, all kinds of fibrous waste, shearing fluff.

*Dangerous liquids*: all liquids that, at the ordinary temperature, liberate inflammable vapours which form explosive mixtures with air, namely, carbon disulphide, ether, acetone, (hot) alcohol, wood spirit, lacquers, varnishes, benzol, petroleum spirit, illuminating oils.

*Carriers of Oxygen (q.v.)*: all substances that readily part with oxygen, such as peroxides and peracids.

The substances in heavy type should not be stored with those mentioned after them in each section of the following list:—

**Organic Substances**, with nitric acid, carriers of oxygen, ozone, peracids, picrates, chlorates, liquid air, fulminates, fats or oils.

**Lampblack or Carbonaceous Substances**, with fats, oils, sulphur, metallic sulphides, or carriers of oxygen.

**Metals in Powder, Bronzes**, with damp substances, water, dusty materials, mineral acids, ethereal or fatty oils, oil of turpentine, carriers of oxygen, ozone, liquid air, peracids, or flowers of sulphur.

**Peracids**, with organic substances, sulphur, metallic powders, bronzes, carbon, or dangerous liquids.

**Resins, Turpentine, Ethereal Oils**, with iodine or chlorine, mineral acids, carriers of oxygen, or dangerous liquids.

**Carriers of Oxygen, Liquefied Oxygen, Ozone**, with fulminates, chlorates, organic substances, picrates, bronzes, metallic powders, dangerous liquids, carbon, lampblack, resins, phosphorus, sulphur, sulphuretted hydrogen, nitric acid, or dusty substances.

**Dangerous Liquids**, with carriers of oxygen, ozone, liquefied oxygen, oil of turpentine, ethereal oils or peracids.

**Carbides and Quicklime**, with water, damp substances, or acids of any kind.

**Strong Nitric Acid**, with oil of turpentine, hydriodic acid, organic substances, sulphuretted hydrogen, carriers of oxygen, ozone, carbides, metallic powders, bronzes, strong sulphuric acid, fulminates, picrates, or chlorates.

**Strong Sulphuric Acid**, with strong nitric acid, saltpetre, substances impregnated with saltpetre, metallic powders, bronzes, carbides, picrates, fulminates, or chlorates.

**Carbon Disulphide**, with carriers of oxygen, ozone, or liquefied oxygen.

**Fulminates, Picrates, Chlorates**, with mineral acids, organic substances, sulphur, carriers of oxygen, ozone, or liquefied oxygen.

**Dusty Materials**, with metallic powders, bronzes, carriers of oxygen, ozone, or liquefied oxygen.

**Sulphur, Metallic Sulphides**, with carbon, lampblack, fats, oils, chlorates, or phosphates.

**Water (Solutions), Damp Substances**, with quicklime, carbides, metallic powders, bronzes, light metals.

**Phosphorus**, with chlorates, carriers of oxygen, ozone, or sulphur.

**Nitrates and Substances Impregnated with Saltpetre**, with sulphuric acid.

**Fats, Oils**, with organic substances, lampblack, carbon, metallic sulphides, or pyrites.

The following substances should be isolated during storage: all those mentioned in the Appendix on Dangerous Properties and Reactions, as spontaneously igniting or explosive; all firework charges, nitrated cellulose, fulminates, detonating compounds, chlorates, picrates, peracids, igniting pellets, gunpowders, metallic nitrides, nitrogen iodide, chloride, fluoride, and bromide, the dangerous peroxides (*e.g.* hydrogen peroxide and potassium peroxide), liquefied gases, and phosphorus.

To complete the arrangements for ensuring protection from fire in all premises, the provision of rational means of fire extinction is essential. Of course we do not intend to discuss the tactics pursued by Fire Brigades in dealing with conflagrations, but merely to briefly indicate methods calculated, in many special cases, to retard the further chemical extension of flame in burning substances, for which purpose water is not always useful, and may indeed occasionally have a stimulating influence on the progress of the fire.

In some fires the employment of water may be very dangerous, and its use should be prohibited under all circumstances where:

- (1) It may favour the progress of chemical reaction,
- (2) It assists the spreading of the burning substances, and
- (3) It may effect the liberation of dust.

With regard to the first category, certain substances, whether cold or hot, enter into violent chemical reaction on contact with water, and generate an extremely high temperature, or liberate dangerous compounds or explosive gases. Such substances include quicklime (in contact with water develops considerable heat, up to red heat, 800° C.), whilst carbides liberate the explosive gases acetylene or methane. Light metals disengage explosive oxyhydrogen gas or hydrogen from water, and the same effect is produced by red-hot metals and bronze powders (see *Metals*).

Secondly, substances lighter than, and incapable of mixing with, water must on no account be quenched with that liquid when burning,

because instead of diluting them, the water acts as a carrier and facilitates the extension of the fire. Moreover, the heat of combustion of these substances is usually so great that the quenching action of water is very slight; they comprise ether, carbon disulphide, benzol, fats, oils, mineral oils, ethereal oils, lacquers, varnishes, resins, paraffin, naphthalene, tar, tar oils, wax, sulphur, ozokerit, and ceresin.

In the third contingency, when dusty, pulverulent materials, in presence of fire, are sprinkled with water so that clouds of dust are produced, and these latter remain suspended in the air for some time, very dangerous explosions of such dust may ensue. Dangerous clouds of dust are furnished by all kinds of flour, lampblack, coal, sawdust, cellulose powder, celluloid powder, metallic powders, bronzes, dried plants, drugs, pigments, agricultural fodders and fertilisers, bran, grist, malt culms, waste from purified products, wool dust, wool waste and waste from fibres, dextrin, sulphur, naphthalene, and powdered sugar (see *Dust Explosions*).

In all three eventualities, the use of water in quenching fires must be avoided, or only practised with extreme care.

The numerous commercial fire-extinguishing preparations, which are designed for special purposes, are only successful when circumstances enable their quenching influence to be developed, and when their composition is suited to the chemical processes coming into play.

An otherwise very good extinguishing agent, capable of counteracting flame or incandescence by the liberation of gas or vapour, can only be used in closed rooms or places where its active ingredients are prevented from dissipating. Fires in open places, where the draught set up by the fire itself comes into play, can never be successfully combated by such means, the gases or vapours being diluted too greatly to be effective.

Furthermore, the chemical composition must be suitable for the object in view. Unfortunately, as in the case of boiler fluids and insulating compositions, entirely useless extinguishing agents, of arbitrary composition, are often put on the market at high prices, and vaunted as suitable for fires of all kinds. Indeed, some of these preparations contain ingredients actually calculated to spread rather than extinguish fire. This applies more particularly to those containing saltpetre or nitric compounds, the high percentage of oxygen present feeding the flame, whilst the nitrous gases evolved prevent access to the seat of the fire.

It is better to abstain from purchasing chemical extinguishers, and to prepare them oneself, where circumstances indicate their employment as useful, *i.e.* in small, enclosed rooms; and in such event a supply of the extinguisher should be kept close at hand ready for use.

The suitable chemicals will be given later on.

The action of water in fire extinction is well known, namely, quenching accompanied by a cooling of the burning or endangered objects. The latter can only burn when raised to combustion temperature, and this is prevented by the water.

In addition, water acts by the liberation of steam, which displaces the air and deprives the flame of the oxygen necessary to its existence, and at the same time the considerable quantity of heat consumed in the formation of this steam is extracted from the burning objects, so that a

cooling effect is produced—first by the direct influence of the water, and secondly by the extraction of heat in forming steam.

High-pressure steam, delivered to the seat of the fire direct from a steam generator, is far more efficacious than ordinary water vapour. Such steam acts in virtue of its expansive power, whereby the atmospheric oxygen is displaced from the vicinity of the burning object with such violence that the fire dies out from lack of oxygen. The action of high-pressure steam is particularly noticeable in closed rooms; and such steam is suitable for extinguishing any kind of fire, except under circumstances referred to above under (1). If any establishment is provided with a steam generator and the necessary pipes, the problem of fire extinction in these premises may be regarded as solved, provided the attendants appointed to look after the appliances in question do their duty.

However useful the physical action of steam may be in quenching fire, it must not be expected, any more than water, to withstand chemical influences; *i.e.* it must not be employed under circumstances that will lead to its decomposition into its chemical constituents, since under these conditions both steam and water may prove a grave source of danger, and develop from an extinguishing agent into an explosive substance. Both water and steam furnish the readily inflammable gas, hydrogen, which, in conjunction with oxygen or air, forms oxyhydrogen gas. This latter will explode, even at  $700^{\circ}\text{C.}$ , on exposure to any flame or spark. Now, as all glowing ironwork, girders, pillars, &c., will have a temperature of  $680^{\circ}\text{--}1000^{\circ}\text{C.}$ , any such articles present at the seat of a fire will be in a position to decompose water or steam, and thus liberate the oxygen and hydrogen necessary to the formation of the explosive mixture aforesaid, which may then be the cause of enormous damage (see *Metals*).

The quenching action of water may be considerably augmented by the addition of certain salts, which either dissolve or remain in suspension in the liquid. The efficiency of such salts resides in their capacity for absorbing heat, which they extract from the burning objects, and thus cool the latter down below the combustion point. They economise water; an important matter at the commencement of a fire, since it is usually at this stage that the water supply is least abundant.

Another manner in which these saline substances act is by forming a more or less incombustible incrustation on the surface of the objects with which they come in contact,—thus preventing the spread of flame. In the case of half consumed objects, the incrustation also diminishes the risk of the fire breaking out afresh. A double value, for the purposes of fire extinction, is possessed by salts that not only form a fireproof incrustation, but also liberate flame-suppressing gases and vapours like carbon dioxide, ammonia, and sulphur dioxide.

Apart from these fire-extinguishing agents of simple composition, there are others, composed of several ingredients that must be stored separately and only mixed at the moment of application. These agents are known by special names and packed in special vessels (fire bottles or hand grenades), which break when thrown into a fire or exposed to heat, and liberate their contents, which then exert a quenching effect. These “artificial fire extinguishers” are open to the objection of being too “chemical”; on the other hand, they harmonise with the theory of fire extinction, and may, when properly used in the right place, occasionally

do good service. Nevertheless the same results could be produced by a few buckets of water, and at a much cheaper rate, these chemical extinguishers being usually very expensive.

After these general observations, the following brief remarks on industrial fire-extinguishing agents may suffice:—

The cheapest, whilst at the same time very efficacious, adjunct to water for quenching fire is fine clay or loam, water containing this substance in suspension being far better able to extinguish fire than when pure.

Water glass (sodium silicate) is very useful, but corrodes the pumps. It must always be stored separately, in tightly closed receptacles, and only added to the water just before use. Soluble phosphates, ammonia salts, crude soda and potash, boric acid, Stassfurt salt, manurial salt, common salt, calcium chloride and magnesium chloride are all very good, some of them liberating fire-quenching vapours. Being very cheap, they can be added to the water in large quantities. In the case of fires where great heat is generated, the five last-named ingredients disengage no small volumes of chlorine and hydrochloric acid gas, which, though acting adversely on flame, retard the work of extinction in closed spaces by rendering the atmosphere unbearable.

Alum and Glauber salt are also efficacious, though less so than the others mentioned, and are only used in case of need. Saltpetre and substances containing nitrates should be discarded entirely for the purpose in view, since they merely kindle and feed the flame, and, by liberating poisonous nitrous gases, retard the work of fire extinction.

Compound extinguishing agents, the components of which must be stored apart, and only mixed immediately before use, usually act by liberating flame-quenching vapours; they are not always reliable in practice, are expensive, and only suitable for use in small rooms. Slight accidental circumstances often render them quite useless. To this class of agents belong a number of complicated appliances (of the "Excelsior" type); some of them consist of an acid and a solution of a carbonate, isolated from each other in glass tubes. At the instant of use the tubes are broken, or the acid and solution are brought into contact by some other means, whereupon carbon dioxide is liberated under considerable pressure, and mingled with the water, which it forces out of the apparatus. The pressure may attain as much as six atmospheres. The appliances are often very useful, specially at the *beginning* of an outbreak; but when they have been kept for some considerable time they are liable to get out of order. For instance, the unavoidable evaporation of the water, or the use of too strong a solution, may result in the crystallisation of the salts, in which case the crystals are likely to obstruct the mouth of the apparatus; or again the gas pressure may be developed so suddenly as to burst the vessel (see *Chemiker Zeitung*, 1902, Nos. 15 and 38).

Apparatus of this kind should never be kept too long, or exposed to excessive cold, on account of the danger of crystallising or freezing, being then liable to fail in the hour of need, and prove a greater danger to the user than useful for the work in hand.

The quantity of the aforesaid agents amounts to 5–10 per cent. of the water employed. It is advisable to keep a strong solution ready prepared (to save time at the critical moment), and dilute this to the working strength when the occasion arises, *i.e.* on the outbreak of fire.

The solutions should be stored in glass vessels exclusively, and these latter should be of such a shape that, if necessary, they can be thrown direct on to the seat of the fire. The vessels must be brittle, and not too large to be conveniently thrown from a distance on to the seat of the fire, or on the places to be protected. The throw must be sufficiently powerful to break the vessel.

It is almost useless to employ these grenades and similar appliances in the open, or in the case of large fires. Their effect is also small in the case of very combustible substances, such as large quantities of straw, hay, seaweed, flour, &c.; for one reason, because the softness of the material protects the flasks from breakage, and they only burst afterwards under the influence of the heat. This defect, however, may be overcome by notching the glass with a file before throwing it into the fire. On the other hand, their employment is advisable in enclosed spaces, corners, passages, shafts, &c.; and under these favourable conditions a pint of solution will do as much good as ten times the quantity of plain water.

In cases where water must not be used for extinguishing fire, these saline solutions are also inadmissible, since the salts do not prevent the dangers caused by the water, except where the fire is of such slight extent as to be extinguishable by the impact of any small substance.

The best fire extinguishers are those of a gaseous character: carbon dioxide, sulphur dioxide, and ammonia. These are even superior to steam, inasmuch as, unlike the latter, they do not furnish explosive gaseous mixtures under certain circumstances, *e.g.* in presence of glowing metal, lime, carbides, light metals, bronzes, &c. The liquefied gas industry is now in such an advanced condition that it is easy for all premises to keep a stock of these proved quenching agents. A small bottle, that takes up very little room, and for which a convenient place is easily found, will furnish a large volume of gas, which can be conveyed through pipes to any room specially endangered in the event of fire, and stifle any outbreak of flame. Such an arrangement is most efficacious in case of fires in enclosed (even large) rooms, cellars or stores, which contain explosive materials, and therefore cannot be entered owing to the fear of explosion. Gaseous extinguishing agents also exhibit the great advantage of not damaging the goods like water does; and they likewise afford the greatest protection against the risk of the fire breaking out afresh, or of an after explosion.

When a fire has been extinguished by the brigade in the usual manner, a possibility arises of the fire breaking out again, or an explosion ensuing, through the gasification of still unconsumed materials under the influence of the heat in the ashes and débris. This danger is specially imminent where dangerous liquids are in question, but can be entirely obviated by the right use of extinctive gases, since these latter stifle all incandescence, and even where the interior of the débris is still glowing, the gases are able to penetrate and drive out all oxygen, thus extinguishing the flame and glow.

Of the three gases mentioned above, carbon dioxide is to be preferred, being cheaper, more easily obtainable, and safer to work with than the other two, both of which are far more dangerous to man. When present in sufficient quantity (about 10 per cent. is enough) carbon

dioxide — and in some instances sulphur dioxide as well — will render explosive mixtures of air and gases harmless.

The employment of these gases against fire is an exceedingly simple matter. The gas bottles or cylinders (see *Liquid Gases*) must be kept in appointed places, where they cannot be affected by fire or the ordinary work of the premises. They must not be exposed to the sun or to any source of heat, but be kept in a cool place, because heat renders them liable to explode; and they must also be readily accessible.

Pipes must be provided, extending from the gas cylinders to the specially endangered parts of the premises, and these pipes should debouch close to the floor, not at a high level, since, however dense the gases may be (and sulphur dioxide is 2·10 times as heavy as air, carbon dioxide  $1\frac{1}{2}$  times, and ammonia only 0·5 the density of air), they will never be able to overcome the updraught produced by the fire, but must be introduced at a low level and be conveyed by this draught to the seat of combustion.

The tests made some time ago by C. Mönich of Berlin to extinguish fire with carbon dioxide proved a failure, because the experimenter, starting with the erroneous assumption that the dense gas must necessarily descend through the burning fire and stifle it, introduced the carbon dioxide into the test hut from above.

The quenching power of carbon dioxide is considerable, but the minimum effective quantity varies with the kind of flame, some requiring more, others less.

The following list shows the amount of carbon dioxide, in proportion to the oxygen present, needed to extinguish the flame produced by the combustion of:—

	Carbon Dioxide.	Oxygen.
	Per Cent.	Per Cent.*
Marsh Gas . . . . .	2·3	15·6
Paraffin Oil . . . . .	3·0	16·6
Candles . . . . .	3·2	15·7
Alcohol . . . . .	4·3	14·9
Coal Gas . . . . .	4·9	11·3
Carbon Monoxide . . . . .	12·25	13·3

\* The remainder is nitrogen.

To be capable of quenching fire it is not necessary for the carbon dioxide to be in a pure state. Combustion will cease, in the following cases, when the ordinary air contains the percentages of carbon dioxide stated below:

10	per cent.	in the case of marsh gas flame.
14	”	” candle flame.
15	”	” paraffin oil flame.
16	”	” rape oil flame.
24	”	” carbon monoxide flame.
33	”	” coal gas flame.
58	”	” hydrogen flame.

These figures sufficiently show the divergent minimum percentages of carbon dioxide necessary to the extinction of different kinds of flame.

When a fire, in an enclosed space, has been extinguished by the aid of gas, it is necessary to allow the gas to continue to act on the débris for some time, in order to thoroughly stifle any remaining incandescence and prevent any subsequent effects from the accumulated heat.

In isolated instances of fire, certain liquids have also proved efficacious, *e.g.* milk, chloroform, carbon trichloride, and even the dangerous carbon disulphide. Their special application will be mentioned later on.

In all cases where water is inadmissible, dry fine sand is suitable; but there must be an abundant supply, kept in the right place. This material (also ashes or dry earth) is thrown on to the seat of the fire. Once used, especially when fires of oil or resin are in question, such sand, &c., should be thrown aside, not employed again.

For extinguishing fire in special cases, the following substances and methods have proved most useful:—

Petroleum fires (water must never be used!):—

In the open: milk, ammonia, chloroform, carbon trichloride, sand, ashes, earth, soaked bags and cloths;

In closed rooms: exclusion of air, introduction of quenching gases and steam;

In tanks, &c.: putting on the covers.

Fires of oil, fats, mineral oils, waxes, ozokerit, tar, resins, lacquer, varnish, carbon disulphide, alcohol, ether, benzol, acetone, wood spirit, and similar substances:—

In the open: application of sand, earth, ashes, bags, and cloths;

In closed rooms: exclusion of air, introduction of quenching gases or steam;

In tanks: putting on the covers;

In these cases, also, water is inadmissible.

Fires concerning acids, acid carboys (*q.v.*), nitrating liquid:—

Water must be used in all cases; never sand, earth, or even ashes. Tan, sawdust, or organic substances will only feed the fire.

Fires of gases, vapours, mixtures of air with gas or vapour:—

In the open: chloroform, carbon trichloride (a very expensive remedy!);

Indoors: steam, exclusion of air (also closing the ventilators);

In tanks: putting on the covers.

Fires in the centre of coal heaps:—

At the outset: dividing into smaller heaps (surface cooling);

In advanced stages: water, but only in the event of a sufficient supply being available to thoroughly drench the whole heap; partial quenching will merely favour the progress of the fire.

Fires in general, when large masses of glowing iron or other metal are present (foundries, iron buildings):—

Water should never be used, owing to the danger of forming oxygen-hydrogen gas. Where it is impossible to enclose the seat of the fire the incandescence cannot be stifled by any known means; otherwise carbon dioxide is useful.

Fires in chimney stacks:—

About 4 ounces of carbon disulphide, or thin sulphur sticks (the former being preferred, as burning quicker), are ignited on a fireproof support at the bottom of the chimney, the liberated sulphur dioxide then

putting out the fire. Care must be exercised when carbon disulphide is used, and the work must never be entrusted to unskilled hands.

Fires in waste heaps, dumped soda waste, pyrites, or substances containing metallic sulphides :—

In the advanced stage (mostly internal conflagrations) water must never be used, on account of the risk of oxyhydrogen gas being formed, and of the liberation of combustible sulphuretted hydrogen.

Furthermore, when extensive heaps take fire there is nothing to be done but to stop up all openings, so as to prevent access of air. Small heaps should be opened out, thrown apart, and then quenched with water, if surface cooling does not effect the desired result.

## CHAPTER VI

### INVESTIGATIONS AND PRECAUTIONS IN CASES OF FIRE

#### Incendiarism

It is oftentimes a matter of interest to fire insurance companies, judicial authorities, the police, the fire brigade, and the occupier of the premises to ascertain the cause or origination of a fire. The insurance company desires to know whether it is liable under the policy; the authorities, whether the case is one of incendiarism; the brigade, how a recurrence of the fire can be prevented; and, finally, the owner of the goods is anxious to determine the cause, in order to adopt preventive regulations for the future. Very often, however, it is impossible to obtain the desired information as to the origin of the outbreak; and indeed, between the years 1878 and 1889, the cause of 34 per cent. of the total number of outbreaks proved untraceable.

The causes of fires in dwelling houses and agricultural premises can readily be ascertained; sometimes a malicious hand, at others an accident, in other cases, again, structural defects, juvenile carelessness, or the thoughtless handling of lights or fire are the causes. In such cases the usual investigations pursued by the representatives of the insurance companies are sufficient, and no further steps are taken, the companies recognising the fact that fires of this class cannot be entirely prevented, even when more stringent conditions are laid down. Such fires belong to the accidents of daily life, and it is very difficult, indeed impossible, by imposing stricter regulations, to infuse more caution into the insured, who are rendered careless by the fact of their being insured and of having a legal claim to be reimbursed for the damage done by fire.

The circumstances are different in the case of factories, where the nature, condition, manipulation, storage, and mixing of numerous raw materials, intermediate products, manufactured articles, waste products, &c., as well as the labour, attendance on machinery, firing, lighting and heating, occupy a far more prominent position; where, in addition, the presence of numerous workpeople and strangers has to be taken into account; and, finally, where new and unknown substances have to be

converted by equally unknown or secret processes into new products, dangerous operations are performed, or where prohibited measures may perhaps be resorted to for the sake of pecuniary advantage.

Under such multifarious and constantly fluctuating conditions, the determination of the cause of outbreaks of fire becomes both important and difficult; in such cases the outbreak is not necessarily due to the causes already mentioned, but frequently to chemical reactions, occurring (and unpreventable) in the course of the work, or during the storage of the materials and adjuncts of same.

In such fires, where human agency is less in question than the chemical activity of the materials, or the lighting or heating plant, the usual methods of investigating the cause of the outbreak are insufficient, and require to be extended to an examination of the nature and mutual behaviour of the materials present, the condition of the damaged substances, ashes, débris, &c., in order to discover the form of chemical activity causing the fire.

In this direction much has already been accomplished by the aid of chemistry, but in view of the frequency of problematical and inexplicable fires and explosions in chemico-technical establishments, the experience gained and discoveries made, more particularly in explosions and cases of spontaneous ignition, must be considered as relatively insignificant and insufficient.

To attain greater success than hitherto possible in ascertaining the causes of such fires, and devising means for their prevention, it will first be necessary to accumulate a whole series of practical experiences and observations, compiled separately for each class of works and materials, by experts. The first step to be taken in this direction is the acquisition of the chemico-technical knowledge requisite for conducting observations on the progress of fires and for adopting precautions at the seat of such fires, which precautions primarily consist in the proper sampling of substances which, when subjected to physical and chemical examination, are likely to furnish information respecting the nature of the fire. Such samples should be taken during the progress of the fire if possible, or at any rate shortly after, especially when the cause of the outbreak seems problematical from the outset.

In the event of an explosion causing the fire, or occurring during its continuance, it is essential to ascertain: (1) what gases, vapours, or kind of dust are generated, used, or discharged by the operations practised in the works; (2) what was the force exerted by the explosions, what the effect produced on timbers, walls, apparatus, and machinery, and how far any objects have been hurled by the explosion; (3) what alteration (distortion or breakage) has been produced in metallic fittings; (4) whether the walls have been driven inwards or outwards by the force of the explosion; (5) at what place the explosion occurred, and what special operations were carried on, materials stored, or appliances used there.

The accurate locating of the seat of the explosion is a matter of great importance, especially when explosions of gas, vapour, or dust are in question. This enables one to fix the distance of the spot from the nearest open fire, light, or heating appliance, and also the distance from any place where inflammable gas or vapour was produced. Another point to be determined is the kind of intervening structures between

the two places: walls containing windows, doors, ventilating apertures, free spaces, stairways, corridors, &c., and what effect has been produced on the same by the explosion.

No less important is the determination of the relative altitude of the two spots aforesaid; whether the seat of the explosion is situated at a higher or lower level than the starting point of the inflammable gas or vapour, or the position occupied by the open fireplace. These altitudes must be considered in relation to the density of the gases or vapours in question.

When the state of the fire allows, an examination of the damage done by the explosion to the objects between the seat of the explosion and the starting point of the gases or the situation of the open fireplace should not be omitted.

When two or more walls have been driven together by the explosion, and not, as frequently happens, forced outwards, it is probable that the damage has been produced by an explosive of great disruptive power (see *Gas Explosions*).

The site of the fire must be thoroughly investigated, as also any unconsumed objects present, samples being taken of the latter. The examination of the site is for the purpose of ascertaining:

(1) The presence of any extraneous bodies not belonging to the work or materials treated on the premises, and comprising articles or materials which, although kept or used in the establishment, have no business to be in the place where they are found. For instance, oil-cans discovered in a part of the works where there is no machinery or machine parts requiring oiling. Other substances to be classed in the same category are such as have been entirely changed in their shape or character by the cause of the fire, *e.g.* fused iron or glass when no degree of heat sufficient to fuse them has prevailed on the spot during the continuance of the fire itself.

(2) The presence of substances capable of spontaneous ignition or easily brought into that condition, and therefore able to set fire to other readily inflammable substances; these include quicklime, carbides, metallic potassium, metallic sodium, and all the substances cited in Table I. of the Appendix as liable to spontaneous ignition.

If the goods stored or treated on the premises are known, it should be ascertained whether they could have produced spontaneous ignition or explosion during their treatment, or by accidental admixture or contact in storage.

(3) The state of combustion of the objects, the appearance of damaged objects and their ashes.

In this case attention should be bestowed on the appearance, degree of moisture, dryness or carbonisation, percentage content of fat or oil, smell of the burnt objects. To estimate the intensity of the heat an examination is made as to how far its effects have penetrated into the burnt objects, *i.e.* the relative external and internal appearance of these latter. Any closed vessels that have been standing in the fire should be left unopened until cool inside. This is essential as a matter of precaution, since, if vapours have been generated in the interior of such vessels, or their contents undergone partial carbonisation, the admission of air, by opening the vessel, may lead to spontaneous ignition or even explosion, and thus entail the loss of a piece of evidence.

The condition (and eventually the tendency to spontaneous ignition) of the insulating material on steam pipes and other conduits should be examined. The colour and nature of the ashes must be carefully determined. Many organic substances, though readily inflammable, are incinerated with difficulty, *i.e.* they furnish a black or dark-grey ash. When the ashes of such materials (paper, textiles, fibres, tobacco, sugar, fruits, herbs, agricultural fodders, &c.) are present, but remarkably white in colour, one may assume the presence of some substance favouring combustion; a carrier of oxygen (*q.v.*), a nitrate, or the collaboration of some readily inflammable liquid (ether, alcohol, wood spirit) may have assisted the incineration of materials that otherwise merely char in fire.

The examination should not be restricted to the surface of the heaps of ashes, but extend to the internal portion, right down to the ground or flooring. The amount of ash is by no means unimportant, since it may approximately indicate whether so much material was really consumed on the spot, or whether the fire was started by the combustion of some extraneous, readily inflammable substance.

(4) To what extent the presence of waste materials may have contributed to the outbreak of fire. The substances more particularly in question comprise oil rags, greasy waste of all kinds, fabrics, fibres or bags soaked with saltpetre, drippings of dangerous liquids, waste gases, spent or unused gases or vapours.

It is important to ascertain where and how these different waste materials were laid or stored, and where the fire broke out.

Attention should also be devoted to the question of greasy clothing, and whether the same has been stored in a dusty, unwashed condition, in crowded bins, or suspended in the vicinity of some source of heat (see *Fireproofing*).

(5) Whether the fire has been due to spontaneous ignition.

Where it is specially important to ascertain whether the case is one of spontaneous ignition for which no liability is borne by the insurance company samples must be taken (cases where legal proceedings are in question). This sampling may be of great importance in arriving at a legal decision; but such will only be the case when the samples have been taken with care, skill, and in an unimpeachable manner, and the samples immediately despatched to the chemist, microscopist, or botanist (as the case may be) by whom they are to be investigated.

(a) The sampling should not be confined merely to all burnt objects exhibiting any special appearance, or to such as have sustained any noteworthy alteration in colour, appearance, or general character by the action of other substances, but should also extend to similar objects that have remained unaffected by the fire, in order that comparisons may afterwards be instituted between them.

(b) Samples should be taken of goods, products, and waste materials in every stage of carbonisation; totally unaffected, slightly and strongly charred, and incinerated objects, each class being kept apart.

In addition to the superficial layers, samples should be taken from the midst of the heaps, and, unless it be too late, attention should be bestowed on the temperature of the various strata of the heap, say of bran, sawdust, wool or other fibre, &c. When the samples can be taken with the entire bare hand, and held without producing any insupportable discomfort, the temperature may be estimated as not exceeding

50°-60° C. True, the susceptibility of the hand to heat differs in each individual, and also varies with the time of year; for instance, a given temperature seems higher in the winter than in the summer, and different substances at one and the same temperature produce divergent sensations of heat (take the case of oily and aqueous substances of actually identical temperature).

When the person taking the samples cannot reliably estimate temperature by the hand, a thermometer should be employed.

(c) Should the interior of a heap of burnt material be damp or wet, and the conditions indicate that this condition is not caused by the water used in putting out the fire, or other water, these varying conditions of moisture should be carefully noted when sampling, and an endeavour made to ascertain whether there are any dry strata present in the same heap.

All these samples should be kept quite separate (about 8-16 oz. will be sufficient in each case), and immediately packed into air-tight glass vessels, which must not be reopened until the time arrives for the chemical examination of the contents. Preserve jars, with rubber fittings, are the best for this purpose.

(d) Whilst it is extremely important that these investigations and samplings should be undertaken during the progress of the fire (if possible), or as soon after as may be, a repetition of the same during the work of clearing up the remains of the fire may afford valuable information on the cause and course of the outbreak. In this task of investigation special attention, particularly with regard to the presence of extraneous substances, &c., should be devoted to the spots that have suffered least through the fire.

## PART II—DANGERS CAUSED BY SOURCES OF LIGHT AND HEAT

### CHAPTER VII

#### GENERAL LIGHTING

AN efficient system of lighting may considerably diminish the danger of fire, since the better a factory and its dark corners are lighted up, the easier it is to recognise and remove defects and possible causes of an outbreak. Hence it is advisable for insurance companies to have visits of inspection paid to technical establishments by night as well as by day, in order to see whether the system of lighting is complete. The class of illumination plays an important part in determining the fire risks of any works; and, strictly speaking, it should be made compulsory for every dangerous installation to be provided with a system of lighting in accordance with the work performed and the danger run, particularly in view of the risk of fire incurred when the illumination is insufficient. Though such compulsion would be difficult to enforce in practice, the needs of the case may be partially fulfilled by taking care that the lighting is good and properly controlled, since the risks of a system of lighting that has its weak points may be ameliorated by careful handling, and indeed, under these conditions, the system may be superior to one that is better in principle but carelessly managed.

In the first place, the superintendence, lighting, extinguishing, and fixing of the lights must be entrusted to a single reliable person, the work being, in this respect, placed on a level with attendance on engines and boilers; and regulations in connection with the system of lighting should be incorporated in the rules of the establishment.

The lights must be arranged in such positions as will enable the work-rooms and passages to be fully illuminated in every part, so as to minimise accidents capable of producing an outbreak of fire. In this connection, care should be taken to see that the lighting plant, generally and in detail, is protected from any special dangers appertaining to the work done on the premises, whilst at the same time the most dangerous parts of the premises receive the best illumination.

Furthermore, the lighting plant should be arranged in such a manner as to be sheltered from the principal dangers arising from it, due to other causes of fire and explosion, and that it may continue its functions even for some time after the commencement of an outbreak.

A distinction may be drawn between the following kinds of illuminating flames :—

*Naked or open flames* : those of coal gas or other illuminating gases (gasoline, ligroin, oil gas, acetylene) in open burners ; fatty oils or fats in simple oil-lamps ; candles ; torches ; magnesium wire, and flash lights ;

*Semi-open flames* : gases in Argand burners, gas glow lights, regenerator burners ; the ordinary petroleum lamps with round or flat wicks ; fatty oils in chimney lamps ; electric arc lamps ; spirit and petroleum glow lamps ; lanterns of reliable construction ;

*Semi-enclosed flames* : safety-lamps, of approved utility ; well constructed storm lanterns, which go out automatically when opened ;

*Enclosed flames* : the incandescent electric lamp, secured by a double bulb and wire netting ; external lamps with gas-tight insulation ; luminous paints.

The choice of a system of lighting must depend, to some extent, on the nature of the operations, raw materials, products and intermediate products, vapours, gases and waste products in question. The person in charge of the lighting plant must also bear these considerations in mind, particular attention being paid to the following points :—

All waste, whether scraps of wick, droppings of oil, scraps of cleaning waste, &c., must be collected and burnt immediately ; never thrown away.

The lamps must be cleaned and filled in a suitable safe place before they are lighted.

The lights must be extinguished in a manner conformable to the nature of the illuminant (see *Petroleum Lamps*).

Lighting agents that have been out of use for some time must not be stored in any dangerous place. When again brought into use they must be freed from old oil, &c., and provided with fresh wick and material.

Lights with open or semi-open flame must be situated at least 30 inches away from ceilings, beams, &c., that consist of wood or other inflammable substances.

In premises where the workmen have to see to the lighting, and on this account bring their own lamps with them, the kind and construction of these lamps must be controlled by the management. In particular, the use of dangerous, explosive oil must be prohibited.

The following fundamental laws may be laid down respecting the class of illumination for various businesses :—

(a) Any naked flame system of lighting may be used in establishments dealing with readily inflammable materials in the solid form (raw materials, products, intermediate products and waste substances), provided these materials be neither pulverised nor caused to give off dust, or are gasified, evaporated, or volatilised. Provided also the lights are fixed, and not carried about from place to place, nor exposed to the risk of falling or being overturned ; and, finally, that the rooms are so high and large that the lights cannot appreciably warm the materials in the workroom.

(b) In establishments dealing with materials that readily give off dust, open lights are only permissible when the conditions under (a) are complied with, and at the same time the suspended clouds of dust are

effectually drawn away by a motor-driven fan, or else the apparatus wherein the dust is produced are enclosed so that none can escape.

(c) Where the appliances for removing the dust are defective or non-existent, enclosed lights alone are permissible, if the dust be of an explosive character (see *Dust Explosions*).

(d) For workrooms that are not used for dangerous operations or materials, but are liable to become heated, any kind of lighting may be permitted, provided the illuminant used does not give off any explosive vapours at the temperature prevailing in the said rooms. Thus, petroleum in lamps must not be used when the oil flashes at  $21^{\circ}\text{C}$ . and the room temperature averages  $25^{\circ}$ – $30^{\circ}\text{C}$ . In such cases the use of ligroin, gasoline, benzine or petroleum ether is prohibited, unless the same be mixed with a large proportion of fish oil or heavy oils.

(e) Where the materials used are not dusty or volatile, but are liable to explode under certain conditions, open lights may be permitted, provided the regulations under (a) be strictly observed, and the lights cannot exert any direct heating effect on the materials. For this purpose large rooms are necessary.

(f) Where readily volatile and inflammable gases or vapours are present enclosed lights alone are permissible.

(g) Storerooms containing stocks of dangerous substances and liquids (ether, benzol, wood spirit, carbon disulphide, &c.) should never be illuminated by open or semi-open lights, and even semi-enclosed lights are only permissible under special conditions. Generally speaking, none but enclosed lights should be used. Where, however, these are not available, and the room has to be occasionally lighted, safety-lamps of approved construction may be used.

In the case of safety-lamps the persons carrying same should be thoroughly acquainted with their use, as also with the behaviour of the flame in an atmosphere of inflammable vapours.

Before being introduced into a room that may contain explosive vapours the safety-lamp must be lighted and locked, and must not be reopened so long as it remains in the room.

The person carrying the safety-lamp must devote all his attention to the phenomena occurring in and around the lamp, whilst any work that has to be done must be performed by a second person.

Safety-lamps of approved construction afford complete protection against all explosions of gas or vapour, and consequently the persons concerned need be under no apprehension as regards their own safety. Only in one contingency is the best safety-lamp liable to failure, namely, in presence of carbon disulphide vapour, against which there is no remedy. Rooms containing this substance must be so illuminated by daylight that no artificial lighting is necessary.

It has not yet been properly ascertained how far safety-lamps are applicable in the case of acetylene; the endeavours to construct an acetylene safety-lamp have not met with the desired success.

Any kind of oil may be used in the safety-lamps, but good oil, free from liability to explosion or tendency to smoke, is advisable. Benzine lamps are the best, fitted with internal igniting devices, so that, should the lamp go out, it can be relighted on the spot without being opened. A double gauze should be used to protect the lamp from injury. Lamps of this kind are made by Friemann & Wolf, of Zwickau.

The term "safety-lamp" does not apply to a lamp merely provided with a wire gauze casing, but only to such lamps as have stood the test of practical use and been approved by a Firedamp Committee.

Experiments conducted with safety-lamps show that they may be used without danger in rooms containing explosive gases and vapours, so long as the wire gauze does not get too hot. On the other hand, the lamp will fail if any of the meshes exceed the necessary small dimensions (900-1200 per square inch), if the gauze breaks or gets in holes, or, finally, grows red-hot while in use. The person carrying the lamp must convince himself that the lamp is in perfect order *before* entering the dangerous room, and must also take care not to move the lamp about so violently, while in use, that the flame strikes through the gauze.

The lamp should be held or set down in a position according with the nature of the dangerous gas, &c., present; for instance, in the case of marsh gas (methane), ethane, volatile petroleum gases, hydrogen, oxygen, hydrogen gas, coal gas, carbon monoxide, acetylene, or water gas, the lamp should be held as low down as possible, since these gases tend to rise before they are mixed with air. If, on the other hand, ether, benzol, alcohol, acetone, carbon disulphide or arseniuretted hydrogen be present, it is advisable to hold the lamp higher, since these gases, being heavy, tend to sink to the floor.

These regulations are frequently neglected in storage cellars where dangerous liquids are daily taken out of the storage vessels in presence of naked lights, numerous explosions and fires being the result. In such places (where heavy vapours are in question) a stand for the light should be provided at a high level, and the usual practice of setting the light down on the floor strictly prohibited.

When a safety-lamp burns in an atmosphere impregnated with gas or vapour, the lamp and flame exhibit certain phenomena indicating approximately the amount of gas, &c., present, and the degree of explosion risk existing in the room (see *Gas Explosions*). These phenomena are:

A. When the air contains more oxygen than is necessary to the combustion of the gas, *i.e.* the proportion of gas is relatively low.

1. The explosive gas is in very small amount: the flame of the safety-lamp becomes slightly elongated, and pointed at the tip.

2. The amount of gas is larger: the flame grows longer, flickers, rises above the edge of the wire gauze, curves, reddens at the tip, and smokes a little.

B. When the oxygen present is just sufficient to consume the gas (*i.e.* the most dangerous stage or explosive limit) the same phenomena occurs as under A 2, but in more rapid sequence; then follows ignition of the gas inside the wire gauze, with the formation of a halo (cap) there, the flame being quickly extinguished, but leaving the halo still visible for some time.

C. When the explosive gases or vapours predominate, the air not supplying sufficient oxygen for their combustion. The same phenomena occur as under B, except that the halo is extinguished much sooner.

The most dangerous condition is that specified under B, and when this ensues the room should be quitted immediately. The condition C is less dangerous from the point of view of the explosion risk, but the larger proportion of gas increases the danger of gas poisoning.

### Various Methods of Lighting

Petroleum Lighting (see also *Mineral Oil*).

In using petroleum for lighting purposes the risk of explosion is greater than the fire risk, and we have therefore to deal with extremes. Provided the general precautionary regulations be observed, petroleum lighting is almost entirely free from danger when high-flash oil (48° C.) is used; but in the case of low-flash oil (under 21° C.) that readily gives off explosive vapour, danger is always imminent, despite the best care and attention; and little protection is afforded by precautionary measures.

The chief danger in petroleum lighting resides in the oil, rather than in the construction of the lamps.

It is a well-known fact that carelessness increases in proportion to the frequency of danger, and so less attention is bestowed on the risk of petroleum explosions; it is handled with negligence for lighting, heating, and kindling fire, and in spite of the occurrence of numerous accidents, no decision has been formed to obviate or diminish the risk, once for all, by raising the flashing point of the oil.

It must be admitted, however, that petroleum is not always directly to blame for the accidents, many other factors coming here into play: ignorance and consequent disregard of the danger, unskilfulness, mischance, the undetectable dangerous character of the oil, breakage of lamps, &c.

These risks could be largely obviated by the use of better oil; but so long as the legislature allows dangerous oil (flashing at 70° F.) to be used, the only way to combat the danger is by improving the construction of the lamps.

It may be laid down as a general axiom that greater protection against the risk of explosion is secured by the use of good oil than by good lamps burning inferior oil. The most frequent cause of explosions is the use of inferior oil in defective lamps, the converse being also true. If, however, only one of these factors be good and the other bad, it may be confidently assumed that the number of explosions will be greater in the case of bad oil and good lamps than with good oil and poor lamps.

The most dangerous part of the lamp is the air space above the surface of the oil, since here is found the vapour which is the actual cause of the explosion. The vapour is very easily formed, *e.g.* when the temperature in the upper strata of the oil reaches 86°-95° F., a by no means uncommon occurrence in lighted lamps. Nevertheless, the vapour is harmless enough if its removal is effected in good time.

A good deal can also be done in obviating the risk of explosion by the employment of indirect means, the following precautions being adopted:—

1. Petroleum lamps should never be exposed to the direct rays of the sun.

2. They should never be exposed to a temperature exceeding 77° F., unless the flashing point of the oil is at least 95°-118° F. It may be taken for granted that in rooms where the temperature exceeds 77° F. (*i.e.* at the spot where the lamp is suspended or standing: ceiling temperature!), the flashing point of the oil should be at least 21° (of the Fahrenheit scale) higher than the actual room temperature.

3. The lamps must be of good construction, with high burners.

4. The only permissible way to extinguish the lamp is by turning down the wick a little to reduce the flame, and then blowing *over* the top of the chimney. It is always more risky to blow the light out from underneath, or to turn the wick down very low.

5. Petroleum lamps that have been found to explode in such a manner that the flame was merely extinguished, without shattering the container, must not be used again until they have been fitted with fresh wicks and different oil. Explosions of this kind are by no means rare in lamps that have not become heated but are fitted with defective wicks that do not entirely fill up the wick tube, and thus leave free communication between the flame and the space above the oil in the container. Under these conditions the vapour ascends, comes in contact with the lamp flame, and then lights back to the container, the vapour in which has not attained its full explosive power; hence the flame is merely blown out without shattering the container. If, however, the vapour in the latter has attained its full explosive power, then the lamp explodes.

6. None of the means advocated for removing or diminishing the explosive tendency of petroleum (*q.v.*) answer their purpose in any way. Consequently, it is inadvisable to burn cheap and inferior oil, and rely on the utility of these means to prevent accident.

7. The safest oil to use is water-white oil that does not give off inflammable vapours below 118° F. This class of oil is specially adapted for lighting hot workrooms.

8. Lamps with round burners keep cooler than those with flat ones. The temperature in the latter may rise as high as 122° F., and they are generally more dangerous than the former type.

9. Wicks should be made of well-dried cotton only, and must be thoroughly dried before use, since the slightest moisture retards the ascent of the oil and causes charring of the wick. Wicks of flax, hemp, or jute char readily, and are therefore dangerous.

10. It is already well known, and is therefore merely referred to now for the sake of completeness, that lamps should not be filled whilst burning, that petroleum should not be poured out of a vessel on to a flame or glowing substance, that vessels containing oil for lighting purposes should be free from water, that all petroleum lamps should be set on a firm resting-place, and that hanging lamps are generally safer than stand lamps, but may become more dangerous than the latter if left exposed through the day to the frequently high temperature of a roof or ceiling.

Gas Lighting (see *Coal Gas* and *Acetylene*).

Here a distinction must be drawn between lighting by gas from the main, and gas that is produced on the premises where it is consumed. In the latter case the risk of fire and explosion is greater, because the more easily prepared kinds of lighting gas are generally manufactured from highly dangerous liquids, and are themselves more dangerous than gas from the mains.

Thoroughly purified coal gas from a well managed gasworks constitutes one of the safest illuminants known, since it does not explode with any great violence, escapes are readily detected by the characteristic smell, the pressure in the pipes is low (1–2 inches water-gauge), the gas does not corrode the pipes, and it has a lower density than many other kinds

of gas, a circumstance that considerably facilitates its diffusion and dilution in the air.

The risk of gas lighting has been greatly diminished by the introduction of the incandescent light. In the first place, a far smaller quantity of gas is consumed, and, should the taps be left turned on through carelessness, the waste is reduced. Secondly, the heat radiated by the incandescent light is considerably less than that from ordinary gas flames, which latter may become a source of great danger to adjacent objects, both by the heat disengaged and by their tendency to flicker.

Gas is superior to petroleum as an illuminant by reason of the smaller trouble involved in attention. The danger is smaller, owing to the immovable character of the lights, except table lamps that are connected with the pipes by flexible tubing. In gas lighting there is no necessity for storing a readily inflammable fuel, this task being performed by the gasworks, communication with which can be cut off by simply turning the main tap.

Coal gas (*q.v.*) being readily inflammable is naturally liable to cause certain risks in establishments of a dangerous character, and under such conditions needs greater care in handling. In such cases a Muchall tester should be invariably employed, especially in works where small escapes of gas may cause damage, *e.g.* where much dust is produced. Seeking for escapes of gas with an open light is a very dangerous procedure, and in endangered premises soap solution alone should be used for this purpose (see *Coal Gas*).

In dangerous establishments the thawing of frozen gas pipes or meters with naked flame must be prohibited, the work being done with hot water and hot rags. It should be remembered that it is not the gas but only the water that freezes in these cases.

The small bye-pass flames in common use for lighting incandescence gas burners are open to objection in the case of closed rooms. A very slight circumstance, draught, temporary decrease of pressure, &c., may lead to the extinction of these nearly invisible flames, so that a by no means inconsiderable amount of gas may escape during the daytime. True, in large rooms the quantity will not suffice to produce an explosive mixture of gas and air, but in very small rooms the amount of gas escaping in the course of 10–12 hours may be enough for this purpose.

Moreover, the amount of gas actually required to produce an explosive mixture is not so very large, and the deficiency may be supplemented by any light dust present in suspension in the air. This result will be produced by small quantities of flour, lampblack, cork or wood, in the state of dust; also the dust from various kinds of waste (see *Dust Explosions*).

Just as high temperatures increase the dangers of petroleum lighting, so is the risk of gas lighting augmented by the presence of suspended particles of dust, the danger in both cases being that of explosion.

In the competition between various illuminants, endeavours have been made to elevate gas into a position of superiority by resorting to pressure for increasing the lighting power; and for this purpose a number of appliances, many of a very complicated nature, have been introduced under different names (*e.g.* Millennium light, Lucas light, &c.).

A pressure of 1 atmosphere is sufficient to considerably increase the illuminating power of coal gas, especially in incandescence burners; but the drawback of many of these systems is the necessity for employing a

hydraulic or electric motor. Gas compressed to the degree aforesaid has not a very much greater fire and explosion risk than when under the ordinary gas pressure; but the difficulty is that, to maintain this pressure where a number of burners are in question, the working pressure in the pipes has to be increased to 2-7 atmospheres, according to circumstances; and to ensure safety under such a high pressure, it is essential that all the appliances should be of very strong construction and maintained in order. This applies to the entire plant, taps and all fittings as well. Old pipes and fittings should not be used for conveying or burning compressed gas until they have been thoroughly tested under the maximum pressure in view. Where the pipes conveying compressed gas have to pass for any distance through dangerous rooms, they should always be fitted with a Muchall apparatus.

Another method of improving the illuminating power of coal gas is by the process known as carburetting (see *Carburetting* and *Naphthalene*). Unless performed on a large scale and under careful management this operation is always open to certain objections, especially in small establishments with a limited staff. To this class of illuminant belongs the albo-carbon light (see *Naphthalene*).

As already mentioned, the incandescent gas light is in certain respects less dangerous than ordinary gas flame; it is cooler, does not flicker, is a semi-open light, and consumes less gas. With regard to the lessened disengagement of heat, experiments have shown that, under identical conditions of gas consumption and pressure, the temperature of 1 litre of water was raised as follows by heating for 10 minutes with:

Simple blue gas flame, without mantle	. 21.9° C.	
Gas flame with thoria mantle	. 19.7° C., i.e. 2.2°	} lower.
„ with thoria-ceria mantle	. 16.2° C., i.e. 5.7°	

In the latter case the difference is considerable. When mantles are used the energy in the gas is chiefly manifested as light, but in the ordinary gas flame is transformed into heat; hence the incandescent light is relatively cool. In all cases where good illumination is required in establishments dealing with readily inflammable materials, and electric lighting is not available, the incandescent gas light is the most suitable form to use.

For further particulars see *Coal Gas*.

Where gas lighting is desired, owing to the dangers of petroleum, and there is no central source of supply, recourse is had in factories to the kinds of gas that can be conveniently manufactured from some readily gasified material by heating, vaporisation, blowing-in air, &c.

In such cases the gas is generated on the premises. For the most part the necessary plant is small, can be set up anywhere, and furnishes a gas that is very cheap in comparison with coal gas, whilst giving a brighter light. The materials used are generally of a dangerous character, some of them particularly so, and comprise petroleum, coal tar oils, ligroin, gasoline, benzine, petroleum ether, spirit, &c. The gasification differs in every case, and the methods of use are also various, some being employed direct as gas, whilst others are employed to raise mantles to incandescence.

The simplest method of preparing such gas on the small scale is by means of a lamp containing a sponge, which is impregnated with the

liquid illuminant, and liberates the vapour of same as required. Of course these lamps are not free from danger of explosion; they must be kept in good condition, never filled while alight, and never exposed to heat.

Of these systems of lighting with home-made gas, only a few will be mentioned briefly here; they are all suitable for illuminating yards and open spaces, but less so for enclosed rooms.

*Dürr light.*—This light is produced by feeding petroleum, drop by drop, to a strongly heated generator, and then heating the resulting vapour. The generator should be heated to the proper temperature before the oil is admitted, the heat being then maintained by the aid of a small burner. These heating operations impart a certain danger to the plant. The quality of the oil is almost immaterial; the charge in the generator varies from 2 to 5 gallons, according to size, and is therefore by no means small.

*Washington light.*—This is a petroleum glow light, the oil being vaporised in a similar manner to that just described, and then consumed as gas by the aid of an incandescence mantle.

*Lucigen light.*—Heavy, and therefore less dangerous coal-tar oil is atomised by compressed air ( $\frac{1}{4}$ – $\frac{1}{2}$  atmosphere) in a mixing chamber, whence it is discharged, strongly impregnated with air, for burning. The charge may be as large as 15 gallons.

Under certain conditions of mutual proportion the explosibility of the mixture of atomised tar oil and air may be very considerable; and in order to minimise this risk constant control and careful attention to the apparatus and operation are necessary to maintain the proportions of the mixture within safe limits.

*Penta gas light.*—In this case only more readily volatile mineral oils (occasionally petroleum as well) are gasified, the vapour being burned in admixture with air. The greater volatility of the materials augments the risk of explosion; and the dangers of storing such low-boiling substances (about 98° F.) must also be taken into consideration.

*Ligroin light, Gasoline light* (for these oils see *Mineral Oils*).—Here again the material is vaporised by heat or compressed air, the vapour mixed with air and burned in suitable apparatus. Though less dangerous than the Penta light, these appliances necessitate great care and stringent regulations, especially when they are of older type, the newer models being greatly improved. In these, as in all other apparatus of similar kind, the chief point is to see that the vapour-yielding material has sufficient room to allow for the considerable expansion taking place when heat is applied. As the expansion is accompanied by the liberation of large volumes of vapour, the two together may easily lead to the explosion of the vessel and a violent outbreak of fire. Hence the vessels should never be quite filled, and a safety-valve should always be provided.

The apparatus and accessories must never be exposed to strong heat, and their use must be confined to rooms where the temperature does not exceed 68°–77° F. Filling the apparatus in the cold and then transferring it to a warm room will cause it to explode at once.

The last two illuminants mentioned are endowed with a certain property of self-protection, which greatly diminishes the danger of explosion, inasmuch as they absorb a large amount of heat in vaporising, and

sometimes require to be warmed artificially in order to obtain the vapour. Since this warming increases the explosion risk it must be performed with care, fire heat being avoided and its place taken by indirect heat (steam, warm water, heated bodies). This artificial warming is frequently necessary in cold weather.

*Benzol light.*—Benzol cannot be employed as an illuminant by itself, but is used for carburetting gases and vapours of insufficient illuminating power, and also for enriching coal gas. From one-sixth to one-third of an ounce of benzol to 100 cubic feet of ordinary coal gas will suffice to increase the lighting power by 1 candle. Though this amount appears insignificant, it attains considerable proportions in practice in the case of large gasworks. For example, the smaller addition mentioned above will mount up to the respectable figure of 20 tons per annum in a gasworks producing 350,000,000 cubic feet of gas. The employment and storage of such quantities of benzol adds in no small degree to the danger of explosions in gasworks.

A variety of benzol, specially prepared for incandescence or air-gas lighting, is sold under the name of soline. From 180 to 370 grams ( $6\frac{1}{2}$ –13 oz.) of this substance are taken to each cubic metre (35 cubic feet) of air. Fifteen to twenty per cent. of this mixture will suffice to render air explosive; but the explosibility disappears when the proportion reaches 70 per cent., flashing and combustion taking its place.

Another group of systems of illumination may be termed in general Air-gas Lighting, since the vapours are mixed with air previous to combustion; or the air may be said to be carburetted, *i.e.* rendered combustible by the agency of vapours from volatile liquid or solid hydrocarbons. To this class belong the Sirius light, Hydririne light, Economic light, Air-gas light, &c.

The materials used are the lightest and most volatile constituents of crude petroleum, namely, petroleum ether, rhigolene, &c., vaporised and mixed with air (or oil gas) in a machine that requires to be carefully worked to ensure the proper proportions. The appliances have now been raised to a high state of perfection, and are fitted with a blower (hydraulic or electric motor), a carburettor (wherein the air is mixed with the vapour), and a regulator for controlling the flow and pressure of the mixture into the pipes.

The attendance on these appliances should be entrusted to reliable men only. An important point to be ascertained is whether the carburetting agents are warmed before being mixed with the air, and how this warming is effected, since it may lead to serious explosions. The lighting plant must, of course, be isolated and placed in fireproof rooms, as in the case of acetylene lighting; and the storage of the materials must be properly supervised.

Contrary to earlier expectations, no separation of air and vapour occurs in the apparatus, and experiments have shown that the mixture remains unchanged for a period of 26 days.

Air-gas, properly so called (petroleum ether and air), contains 14–15 per cent. of gas. The explosive limits of the mixtures of this gas with air range from 9 to 26 per cent. of gas. The gas is also known as hydririne, and is used for power and heating purposes as well as an illuminant.

The principle of (the still imperfectly developed) incandescence

lighting with spirit, petroleum, or benzol is analogous to the production of vapours from liquids in closed vessels by the action of a small heating flame, the resulting vapours being ignited and raising to incandescence a mantle like that used in incandescent gas lighting. Though these methods have acquired a certain importance, and have not been attended by many accidents, they must be considered as generally more dangerous than incandescent gas lighting or electric light; on the other hand, they are safer than air-gas with its cumbrous apparatus.

The dangers of the system mainly reside in the liquid used, which, in addition to being kept hot by the small heating flame, is also exposed to the pressure of the resulting vapour. Owing to the risk of explosion attaching to these appliances, which are of the lamp type exclusively and not on a large scale, they must be managed with great skill and care. Apparatus that has got out of order and been repaired must always be viewed with distrust. In some forms the heating flame is extinguished when the liquid has been sufficiently warmed, a simplification which somewhat diminishes the usual risks.

All liquids—*e.g.* petroleum (for the Washington light), benzol, petroleum ether—furnishing vapours for incandescence lighting must be quite free from water, since, should the latter freeze, though only present in drops, it may lead to the stopping up of the pipes, the consequences being an increased pressure in the apparatus and liability to explosions of a highly dangerous character. As a matter of precaution all the apparatus and pipes should be covered with insulating material as a protection against frost.

For self-evident reasons these systems of lighting should be avoided in dangerous workrooms, and confined solely to yards and open spaces, until such time as the progress in the lighting industry shall have endowed them with the necessary perfection and safety, which they lack at present.

*The Electric light* (see *Electric Plant*). The most perfectly enclosed and safest light of all is the incandescent electric light, which may be used in all circumstances, even the most dangerous, without incurring any direct risk. True, the lamps must be protected by a double bulb and wire netting, the unprotected, single bulb lamp being not entirely free from danger in the presence of readily inflammable substances, by reason of the considerable amount of heat it disengages, especially when it has been in use for several hundred hours.

Experiments have shown that a simple incandescent lamp immersed in water will raise 1 litre of that liquid to boiling point in an hour. Again, lamps tightly wrapped in cotton, curtains, &c., soon charred these materials, and even caused some of them to take fire. Such lamps as are enveloped in light fabrics, for decorative purposes, are therefore dangerous, more particularly when they have been painted over with coloured varnish. A sixteen-candle lamp will char cotton in 10 minutes, and a very slight draught will then suffice to set the cotton on fire, the bulb usually bursting afterwards. The illuminating power does not seem to play any great part herein, and it is almost immaterial whether the fabric is wrapped loosely or tightly around the bulb and the metal fittings. Celluloid articles soon explode when exposed to the heat of the incandescent lamp, and for these reasons the protection afforded by a second bulb becomes highly essential.

When glow lamps are broken in presence of explosive gaseous mixtures the filament instantly ceases to glow, but practical instances show that the extinction is not always so instantaneous as to preclude the ignition of the gaseous mixture; hence some further protection is required by the bulb, and this is best imparted by the use of wire netting. When both these precautions are adopted, the incandescent electric lamp is perfect.

The *electric arc lamp*, as a semi-open light, and one that, moreover, generates a heat of as much as  $3500^{\circ}$  C. ( $3500^{\circ}$  at the positive carbon, and  $2700^{\circ}$  at the negative), besides dispersing fragments of glowing carbon, is in some respects more dangerous than an open light like gas.

The arc light should not be used in places where any liability to explosion exists, nor where any readily inflammable substances are present, unless the falling particles of carbon from the lamp are securely intercepted by a catch plate and prevented from further dispersion.

*Candles.*—These present the same dangers as any other portable open light, but there is no risk of their exploding. Candles that are coloured by an admixture of verdigris or certain other metallic pigments (green in particular) exhibit a particular tendency to relight after extinction, instances having been known where, on re-entering a room, the recently extinguished candle was found to be still burning. An investigation showed that the copper salts used for colouring the candle were converted into copper oxide in burning, and that this oxide continued to glow after the candle was put out, which condition was maintained for some considerable time by the liquid stearin or paraffin ascending the wick. The unconsumed carbon of the wick glowing simultaneously with the cupric oxide, and, being steeped with the fatty substance of the candle, ignited at the glowing oxide, and thus relighted the candle. In this manner an outbreak of fire may be caused by leaving an extinguished candle in the immediate vicinity of a curtain, Makart bouquet, or other inflammable material.

### Heat Furnished by Various Systems of Lighting

In certain establishments dealing with easily inflammable substances, which therefore must not be exposed to heat, even the heat given out by lights, the system of lighting adopted must be one that furnishes a minimum of heat. Unfortunately, the choice of a system is frequently made to depend solely on considerations of expense, the proprietor of the works selecting the one that seems to be the cheapest, without considering whether, in point of fire risk, it is suitable for his purpose or not.

The following lines will be devoted to a brief consideration of this by no means unimportant question, premising that, although the results of different experimenters often differ considerably in detail, they all point to the same general end.

The smallest amount of heat is radiated from bluish-white light approximating most nearly to the colour of moonlight; the greatest heat from illuminants emitting red rays; intermediate in this respect are the yellow-coloured light rays.

On the basis of the amount of heat evolved, the various illuminants may be classified as follows, the heat radiated per candle-power by the

lamp fittings being included. The sequence is from that emitting the greatest amount of heat to that which emits the least:—

Coal gas (single-orifice burner).  
 Candles (stearin, tallow and paraffin).  
 Petroleum (flat burner).  
 Rape oil lamps.  
 Coal gas (batswing burner).  
 Coal gas (Argand burner).  
 Petroleum (round burner).  
 Electricity (incandescent light).  
 „ (arc light).  
 Coal gas (Auer incandescent light).

According to Rubner, the various sources of light exhibit the following ratio in respect of the heat emitted:—

Gas, paraffin, petroleum, Argand burners, incandescent electric light, incandescent gas light.

Wedding gives the amount of heat (expressed in calories) furnished by the various illuminants, as:

Coal gas, regenerative burners . . .	2000
„ batswing burners . . .	1995
„ round burners . . .	1000
Petroleum, 14-line burner . . .	960
„ incandescent burner . . .	550
Acetylene, pinhole burner . . .	534
Coal gas, incandescent burner . . .	500
Spirit „ . . .	318
Electricity, arc light . . .	222
„ incandescent . . .	41

(All without reference to illuminating power or consumption, in lamps of the ordinary type.)

On the basis of a uniform illuminating power of 100 standard candles, the following amounts of heat are liberated by:

	Calories.
Coal gas, double-orifice burner . . .	12,150
Candles, tallow . . .	8,100
„ wax . . .	7,960
„ stearin . . .	7,881
„ paraffin . . .	7,615
Rape oil lamps . . .	6,800
Petroleum, flat burner . . .	6,220
Coal gas, Argand burner . . .	4,213
„ incandescent . . .	3,700
Petroleum, round burner . . .	2,073
Coal gas, Siemens burner . . .	1,843
Electricity, incandescent . . .	290
„ arc light . . .	57

A comparison of the heat furnished by the different illuminants, according to the customary methods in use, gives the following order, commencing with the hottest:—

Candles: tallow, wax, stearin, paraffin.

Coal gas: pinhole burner, regenerative burner, batwing burner, Argand burner, incandescent burner.

Petroleum: flat burner, round burner, incandescent burner (this latter is hotter than the incandescent spirit burner).

Electric light: arc light, incandescent light (in view, however, of the usual relative positions of the lighting agents in practice, *i.e.* distance from the objects illuminated, the incandescent light must be regarded as the hotter of the two).

### Carburettng

Many combustible gases, primarily employed for heating, have also to serve for lighting purposes, although really unsuitable for the latter by reason of their low proportion of carbon, in the form of pure hydrocarbons. In order to increase the illuminating power of these gases it becomes necessary to saturate them with compounds richer in hydrocarbons, and thus enrich them with carbon. This process, numerous varieties of which are practised, is known as carburettng, a term that must not be confounded with carbonising (charring or burning out the impurities in animal fibres).

The gases to be carburetted, *e.g.* coal-gas (especially from inferior coal), hydrogen, water-gas, &c., are treated with the vapour of benzol, petroleum ether, naphthalene, paraffin oil, oil, tar, tar oils, and also with acetylene and oil-gas; even air has been carburetted and converted into an illuminating gas (see *Air-gas*).

The operation is performed as follows:—The liquid carburettng agents are spread out over a large surface by means of porous absorbents or special appliances, and then exposed to the gas to be carburetted, the latter being passed through or over the carburettng material, and becoming saturated with the vapour of the same. Another method is to gasify the carburettng material at red heat (500°–900° C.) in a retort, and introduce the product into the gas to be carburetted. If the carburettng materials are already in the gaseous state, *e.g.* acetylene or oil-gas, they are mixed with the gas by simple injection.

In order to utilise high-boiling (cheap) petroleum residue for carburettng gases (for power), it is first warmed up to about 150° C. (Bennett process), which is easily done by the aid of the hot waste gases from the motor, and with less danger than if direct fire heat were employed. Air is next blown into the warmed residue through fine orifices (in the carburettor), and the resulting mixture of air and vapour is conveyed to the motor. The dangerous feature in this process is the frequent emptying of the non-volatile residue in the carburettor, which operation, on account of the explosive vapour in the carburettor and pipes, should never be performed with open lights or flame.

Carburettng increases the fire risk of the establishment, owing to the storage, handling, and gasifying of the readily inflammable carburettng agents; the greatest danger attaches to the operation of hot carburettng in retorts, but cold carburettng is also open to objection, a gaseous mixture being always more dangerous than a simple gas.

The gasification process must be kept under control, the carburettng apparatus mostly working automatically. All parts of the plant that

have to be opened, for charging or inspection, during the progress of the work, exhibit a high explosion risk, since the opening facilitates access of air and the formation of an explosive mixture of gas and air.

A very simple process is the carburetting of coal-gas with naphthalene in the albo-carbon system of lighting. The flame of the gas burner heats a metallic vessel containing sticks of naphthalene and traversed by the inflowing gas, which issues from the vessel laden with the warm vapour of naphthalene. The only danger possible in this arrangement arises from gross carelessness, resulting in the overheating of the naphthalene and leading to detonation; hence the system is not altogether explosion proof, and isolated instances of explosion have occurred in practice.

### Solid Illuminants

(Luminous stone, luminous paint, Balmain's solid illuminant, Bolognian phosphorus, Osann's phosphorus, Canton's phosphorus.)

Certain pigments exhibit luminosity in the dark. For the most part they consist of pure sulphur compounds: barium sulphide, calcium sulphide, strontium sulphide, zinc sulphide. Of late these substances are said to have been successfully replaced by calcium tungstate.

The preparation of these illuminants entails the use of high temperatures (see *Sulphur Compounds*), but as they are not carbonaceous (and should not be so) they are free from the danger of spontaneous ignition, due to carbon, exhibited by the sulphur compounds.

The raw materials are heavy spar, oyster shells, antimony sulphide, compounds of zinc and strontium, and carbon. These are heated to about 1800° C. in a retort, and incinerated until all the carbon is consumed. The only danger of spontaneous ignition in these products arises when they have been imperfectly freed from carbon and are exposed to the air on leaving the retort and whilst still in a glowing state; under these conditions the carbon takes fire.

Although designated "phosphorus," these substances do not contain any of that element, nor does their luminosity emit heat.

For use they are mostly incorporated with some liquid vehicle, and when moulded are placed in candlesticks, &c., and protected by glass, in which condition they are quite safe. To ensure permanence of luminosity the mass must be exposed to sunlight from time to time, whereby its powers are renewed. No dangerous properties are imparted by this treatment.

## CHAPTER VIII

### HEATING

THE use of stoves for heating purposes need not be gone into deeply here, all that is necessary being detailed in the section on *Explosions*. This being the case, the greater attention is merited by the progressively extending system of central heating in industrial establishments, and

systems wherein the calorific power of wood and coal is utilised by indirect means, since the temperatures and pressures here in question are very divergent in their character and dangers.

### Central Heating Plant

The system of central heating is growing in favour even for small establishments, dwelling-houses, hospitals, hothouses, schools, theatres, and drying plant. The object of the system is to heat several rooms, the entire establishment if possible, by means of a single fire; and it is far less dangerous than the ordinary methods, with their numerous fire-places, pipes, flues, ashpits, &c., each of them constituting a source of fire risk. Nevertheless, even central heating is attended with objectionable features in some cases.

In ordinary heating by means of stoves the heat of the fuel is transmitted direct to the air, walls, and contents of the apartment to be heated; whereas in central heating, use is made of a transporting and circulating medium to convey the heat from the central fireplace to the localities to be warmed.

The transporting medium may consist of water, steam, air, or chimney gases; and the mode of application is divided into various systems and sub-systems, which are now enumerated along with the maximum temperatures they afford and their dangerous factors.

**Water.**—(a) *Hot Water Heating Systems.*—(1) Low-pressure system, temperature 95°–100° C.

The heating appliances attain a temperature of about 70° C. They do not scorch or char any superincumbent particles of dust, and the system is free from danger.

To obtain higher temperatures, plain water is replaced by saline solutions, glycerine, &c., by the aid of which the temperature can be raised to 120°–130° C. Provided the saline matters do not corrode the apparatus, this method is also free from danger. At one time this system was known as “anhydrous heating.”

(2) Moderate Pressure Water Heating; temperature 130° C. This is similar in character to the foregoing.

(b) *Hot Water System* (Perkins' system).

(1) Medium pressure system; temperature 130°–140° C.

(2) High pressure system; temperature 140°–150° C. (occasionally 200° C.). In either case the pressure may attain 5 atmospheres. The dust on the radiators and pipes, as also the wooden lagging and wood-work, may be scorched and charred. The water circulates at a very rapid rate, and the risk of explosion is not entirely precluded.

**Steam** (heating by Waste Steam).

(a) Low-pressure system; temperature 102°–106° C.

The pressure being only about  $\frac{1}{2}$  atmosphere, there is no danger.

(b) High-pressure system; temperature 106°–126° C.

The pressure rises to  $1\frac{1}{2}$  atmospheres; danger from overheating is not precluded.

**Hot Air.**

In this case the air employed derives its heat from appliances (furnaces) heated by chimney gases, fire, steam, or hot water.

This system is very useful for rooms where the air requires to be

frequently changed on account of the production of dangerous gases, vapours, or dust; but it is not easy to regulate, and overheating of the iron pipes is no rare occurrence. These pipes, in fact, grow red-hot and emit sparks, thus causing danger of fire.

The temperature may attain  $500^{\circ}\text{C}$ . in the heating appliances, and hence the method is one of the most dangerous of all systems of central heating.

The choice of varieties of central heating is a question that must be settled by a consideration of local circumstances (including the amount of heat required and the class of fuel available) in each case. The attendant dangers are mostly to be estimated, not from the system employed, but from the manner of its application. Thus an apparently harmless system, developing a maximum temperature of  $100^{\circ}\text{C}$ ., but badly installed, with defective fittings and materials, may prove far more dangerous in practice than a high-pressure steam installation of proper construction. Hence, generally speaking, more care should be bestowed on the construction and installation of the plant than on the system itself, and, wherever possible, the temperature of the heating appliances in the various rooms should be kept down to  $100^{\circ}$ – $120^{\circ}\text{C}$ . at the most.

For Coal-dust Heating, see *Coal*.

### Liquid Fuel

The use of liquid heating agents, like tar, petroleum residue (masut), oil, or the distillation products from lignite tar, is attended with less risk of explosion than is the case with coal-dust heating, though it has its objections when the materials consist of too readily volatile mineral oils, which are not only very inflammable, but give off vapours that form explosive mixtures with air.

These liquid fuels are largely employed as supplementary fuel in conjunction with coal, inasmuch as they are sprayed by steam through nozzles situated in the front wall of the firebox, and, on entering the coal fire, are consumed by a powerful smokeless flame, generating high temperatures, similar to those obtained with coal-dust (*q.v.*).

As is the case with lamp oil, so also with liquid fuel, the flashing point should not be too low. Practical experience on Russian river steamers has shown that so long as the boilers are fired with masut flashing at  $158^{\circ}\text{F}$ ., outbreaks of fire are rare; but when masut flashing at  $116^{\circ}\text{F}$ . was employed for some time, such outbreaks were frequent. Hence the first named flashing point should be insisted on.

Masut residue (burning point  $125^{\circ}\text{C}$ .) is now largely used for heating Martin steel furnaces, the fuel being forced, under a pressure of 5–7 atmospheres, from the tanks into an accumulator (*q.v.*), and pumped thence into the furnace fire.

Where only a moderate degree of heat is required (for warming beds, foot-warmers, food, &c.) sodium acetate forms a useful and safe liquid heating agent. The anhydrous salt, which alone is suitable, fuses at  $58^{\circ}\text{C}$ ., which temperature it retains for a considerable time when in the liquid condition. To utilise this heat the fused salt is kept in a closed metallic vessel, along with a little gelatin and gypsum to prevent premature crystallisation. At the end of two hours the temperature is still  $50^{\circ}\text{C}$ ., after four hours  $40^{\circ}\text{C}$ ., and after five hours  $25^{\circ}\text{C}$ . These vessels,

in which the sodium acetate can be fused direct by immersing them in boiling water, are known as "thermophores," and are free from all danger provided the temperature is not raised above  $100^{\circ}$  C. At  $300^{\circ}$  C. there is danger of an acetone explosion. In any event, these thermophores when properly handled are preferable to the ordinary hot sand bags, heating stones, and (explosive) heating bottles, since they can be warmed by simple immersion in boiling water, whereas the others are often so greatly overheated as to scorch other substances (bed fires).

### Gaseous Heating Agents

Particulars respecting the various gases used for heating will be found under their respective headings (see *Water-gas*, *Dowson-gas*, &c.).

In heating by gas, as in the case of dust and liquid fuels, very high temperatures are attained, owing to the very complete (even explosive) combustion of the materials.

When deciding on a system, preference should be given to the one presenting the best guarantee for an accurate regulation of the fuel supply, and satisfactory solid construction.

*Gas stoves* for living and workrooms deserve special mention on account of their growing popularity.

Given proper construction, there is no danger of the stoves exploding whilst in use, though such a contingency may arise when the stove is being lighted. It is not always possible to apply a light directly the tap is turned on, and sometimes the gas issuing from the pipes is already mixed with air. Under these circumstances, or if the lighting of the stove be delayed from any cause, the accumulation of gas and air in the stove will probably lead to an explosion when the light is applied.

The risk of explosion from such an accumulation of gas and air could be easily obviated by the adoption of means for discharging the initially escaping unconsumed gas into the outer air, by making the burner, or burner frame, movable, so that it could be drawn out of the stove before turning on and lighting the gas.

A further risk of explosion through the escape of unconsumed gases is imminent in certain forms of gas stove with horizontal flames, *e.g.* reflector stoves. If the gas pressure sink too low to maintain the flame strictly horizontal, the possibility arises of an escape of unconsumed gas, which may lead to an explosion.

Should the gas flame impinge on the outer casing of the stove the latter is liable to become overheated (about  $300^{\circ}$  C. or more), and may cause an outbreak of fire. Hence all the metal casing and fittings of gas stoves should be placed far enough away from the flame.

In gas stoves of normal construction the outer case does not get hotter than about  $120^{\circ}$  C. at most, and the gaseous waste products of combustion should not escape at a higher temperature than  $60^{\circ}$  C. As a matter of fact, however, the temperature of the gases is often as high as  $150^{\circ}$  C., which means a considerable waste of heat, to the prejudice of the room that is to be warmed.

Provided the gas stoves are of good construction and well attended to, the system cannot be characterised as dangerous.

Escaping gas is quickly detected by the smell; but this indication is absent in the case of water-gas and Dowson-gas, and therefore these two

gases are more dangerous than coal-gas, unless a smell is imparted to them by the addition of mercaptan, &c.

### Charcoal Stoves

These stoves are like closed chafing dishes, and are fed with charcoal fuel prepared by impregnation with some carrier of oxygen, such as salt-petre, which enables the fuel to glow and consume without the emission of flame. They disengage a quantity of carbon monoxide (*q.v.*), which may become explosive when mixed with air. The store of prepared fuel must be well protected from any sparks or flame, since it readily ignites and glows in an almost imperceptible manner.

## CHAPTER IX

### HEATING BY STEAM

Of all means for transmitting heat, steam is the one most widely used in industrial establishments. From the boiler or steam generator it is conveyed through pipes (often tortuous and of considerable length) to all parts of the works, to be used in some places for heating rooms (radiators), in others for boiling liquids, driving machinery, dissociating solid substances, evaporating, and for lifting or forcing liquids.

Great progress has been made in this application of steam, the temperature and pressure, in particular, having been considerably augmented by improvements in superheaters, boilers, and steam-engines respectively. But though these improvements ensure an increased economy and utilisation of fuel for the manufacturer, they have also heightened the risk of fire and explosion from the insurance companies' point of view.

A distinction is drawn between three kinds of steam, viz. :

Moist steam, containing fine particles of water ;

Saturated steam, free from water in the liquid form ;

Superheated steam, that has been raised to a higher temperature than that of its formation by artificial heat. Such steam is considered slightly superheated when the temperature reaches  $200^{\circ}\text{C.}$ , and strongly so when it attains  $600^{\circ}\text{C.}$  Heating steam above  $600^{\circ}\text{--}700^{\circ}\text{C.}$  is impracticable, since above this point it is dissociated into its constituent elements, hydrogen and oxygen.

### Steam Pressure

The pressure exerted by the air on a superficial area of 1 square centimetre is equivalent to the weight of a column of mercury 760 millimetres high and of 1 sq. cm. sectional area. This column of mercury weighs 1 kilogram (2.2 lbs.), and the pressure of this 1 kilo. per sq. cm. (14.7 lbs. per square inch), constitutes the unit of pressure for steam, namely, 1 atmosphere.

When sufficient steam is generated, by heating water in a partly

filled, closed vessel, to counterbalance the atmospheric pressure on the surface of the water, the steam pressure will be equal to 1 atmosphere. Under normal conditions the attainment of this pressure entails raising the water temperature to 100° C. If the temperature be raised by the application of further heat, the escape of the steam from the vessel being concurrently prevented, then the pressure increases *pari passu* with the temperature as follows:—

Degrees.	Atmospheres.	Degrees.	Atmospheres.	Degrees.	Atmospheres.
80	$\frac{1}{2}$	165	7	195	14
100	1	171	8	200	15
120	2	176	9	213	20
134	3	180	10	220	23
144	4	184	11	230	27
152	5	188	12	365	200
159	6	192	13	375	220

Steam at a temperature of 188° C., therefore, exerts on the walls of the boiler or other enclosed vessel a pressure of 12 atmospheres, or 176½ lbs. per square inch. Conversely, steam at this pressure has a temperature of 188° C.

At the present time the limit of steam pressure in ordinary boilers, and under standard working conditions, is 20 atmos. (213° C.); and in fact it does not seem desirable to go beyond this limit, since at 240° C. steel begins to blue and suffer a diminution in tensile strength. Under special conditions, however, this limit of safety can be considerably exceeded, Laval having, for instance, succeeded in obtaining the almost unheard-of pressure of 220 atmos. (375° C.) by means of a small generator with a minimum of steam and water space, without appreciably increasing the risk of explosion. This steam is used for driving a steam turbine, the vanes of which revolve at a velocity of nearly 3330 feet per second. Up to the present this method of working has not been found more risky than ordinary pressures. Since the working of steam boilers, generators, &c., is controlled by legislative enactments, we shall now merely deal with certain points that are not touched upon in these ordinances.

### Extraneous Substances in Boilers

To minimise the danger of explosion it is necessary that the boiler should be kept free from all extraneous substances that may accidentally gain access thereto, practical experience having shown that tools, boards, nails, and such like auxiliary materials are left in boilers and endanger the plant. For instance, boards and pieces of wood, rendered heavy by the continued influence of steam and pressure, have been found adhering so firmly to the walls of a boiler that the spots covered by these bodies failed to cool, and actually grew red-hot. Under such conditions, explosions are inevitable.

The formation of dangerous gases is also rendered possible by the presence of some extraneous substance in the boiler or steam space. In

more than one case a small quantity of molten zinc from the galvanised steam pipe made its way into the engine cylinder in the vicinity of the boiler. Now zinc and iron, when in close mutual contact and in presence of steam or water, cause liberation of explosive oxyhydrogen gas, and in one instance an explosion from this cause led to loss of life.

The practice of placing a piece of sheet zinc in a boiler, in order to protect the iron plates from corrosion by air in the water, will also lead to risk of explosion should, from any cause, the two metals come into intimate contact.

### Boiler Fur

Another source of danger in the working of boilers is due to the use of improper materials ("boiler fluids") for preventing or removing boiler fur; in fact, instead of curing the existing evil, the water is made more harmful than before. Many waters contain such large amounts of mineral and organic substances that these latter are deposited as soon as the water commences to boil. The deposit settles on the plate, and sometimes sets so firmly thereon that the boiler has to be emptied and the fur chipped off, otherwise the iron under the furred spots, being no longer reached and cooled by the water, gets red-hot, and explosions result. Moreover, furring leads to the expense of stopping work for several days to allow the boiler to be cleaned out.

The number of anticorrosion preparations for boilers is about 200, their ostensible purpose being to either prevent the formation of a solid incrustation, or to facilitate the removal of that already formed. Unfortunately, not one of them can lay claim to be suitable for universal application, owing to the great divergence in the soluble matter in various feed waters; consequently any claim on the part of the makers of these preparations to furnish a remedy for boiler fur, irrespective of the constitution of the feed water, must be regarded as ill-founded. The worst point, however, is that many of them, in addition to being useless, are directly injurious to the boiler, since they contain ingredients that attack the walls, more particularly at the rivet holes, and thus weaken the plates.

In every case the constitution of the feed water should form the basis for determining which is the proper boiler fluid to employ. Furthermore, it is essential to know the exact composition of the fluid itself, whether it contains matters injurious to the boiler, and therefore one should not merely rely on the claims put forward in advertisements.

Any boiler fluid that contains any of the following substances should be discarded at once:

(a) Ingredients that increase the deposit of fur (sand, lime, powdered carbon, or any substances insoluble in water).

(b) Constituents that attack the walls of the boiler direct, or tend to form rust, such as free mineral acids, organic acids, humus acids, sea water, magnesium chloride, chlorine, calcium chloride, sodium chloride (common salt), ammonium chloride (sal ammoniac), ferrous chloride, ferrous sulphate (green vitriol), ammonia, peat, molasses, starch, flour, dextrin, fat, oil, or sugar.

(c) Constituents liable to give off any readily inflammable vapour (tar, tar oils, pitch, nitrobenzol, crude benzol, petroleum, mineral oils).

All the foregoing materials have been detected in commercial boiler fluids.

With regard to the means for removing ready-formed boiler fur, care is also necessary in the selection of these, since many of them (especially those containing tar) burn on to the boiler plate, and thus give rise to explosions, or when brought into contact with the hot fur give off vapours that explode on mixing with air. As the work of removing the fur has mostly to be performed in artificial light, the risk of explosion of these vapours is imminent, and the explosions themselves are mostly of a very violent nature.

According to Savreux, the easiest way to remove boiler fur is by cold water, poured gradually over the walls of the boiler so long as it continues to be warmed by the still hot crust. This operation, which, however, takes time and consumes a good deal of water, is said to soften the fur and enable it to be removed without any risk of injuring the boiler by chipping.

### Water of Condensation

Equally dangerous to boilers and steam pipes is the accumulation of water of condensation in the pipes, as happens when the same are badly laid. This water may cause water-knocks in the pipes, thus subjecting the latter to a pressure that may attain thirtyfold that of the steam present. The greatest sufferers under these circumstances are copper pipes, this metal having a low power of resistance towards high temperatures and pressures. On this account copper pipes are often lapped round with coiled wire, which, however, does not prevent the formation of transverse cracks, but only those in a longitudinal direction. Explosions caused in this manner are quite as violent as actual boiler explosions.

### Superheating

To ensure more complete utilisation, steam is passed through superheaters, wherein it is strongly heated and concurrently dried. The temperature cannot, however, be raised above 600°–700° C., as, when heated further, the steam is decomposed into its constituents, oxygen and hydrogen, which, when mixed together, form the highly explosive oxyhydrogen gas. This danger is, of course, a very serious one, and consequently superheaters must be well constructed and carefully managed. The following general rules should be observed:—

(a) The heating tubes must be made of thick wrought-iron pipe, in length not exceeding 60–80 inches, and supported at intervals of 20 inches.

(b) The diameter of the tubes must be in accordance with the amount of steam to be treated, and must be set so as to be capable of expanding and contracting independently of one another.

(c) The pipe leading from the superheater to the point of consumption should be as short as possible, and protected by a coating of insulating material. All flanges and collars must be carefully packed with fire-proof packing (asbestos) exclusively.

(d) Care must be taken, by providing suitable drainage, &c., to prevent access of water of condensation into the superheater.

(e) The entire plant must be kept under proper control, as well as the temperature and the employment of the steam as motive power, excessive superheating being injurious to the engines; for this purpose, therefore, the superheated steam should be mixed with saturated steam.

All valves, pipes, fittings, and other appliances brought into contact with superheated steam must be composed of some other metal than bronze, since the tensile strength of this alloy is diminished by 4 per cent. at the temperature of 200° C., 18 per cent. at 250° C., 35 per cent. at 300° C., 55 per cent. at 400° C., and 70 per cent. at 500° C.

### Steam Pipes

Steam pipes exposed to any high pressure or containing sharp bends should not be made of copper, since this metal has the highest co-efficient of expansion of all those coming under consideration for the purpose in view. Copper should also be avoided for all pipes that are subjected to continued vibration, as under such conditions the metal quickly loses its elasticity, and cracks or breaks.

Steam pipes of all kinds may become a source of imminent danger to wooden structures and all organic matters (see *Wood*). It must be specially emphasised here that *old* wooden structures and lagging are dangerous in the extreme, and that the circumstance that they have not hitherto taken fire must not be regarded as an indication that they are really fireproof.

In new wooden structures the most dangerous are those composed of wood that still continue to exude resin, this latter charring more easily than the wood itself.

### Insulating Materials

The best way to prevent injury to wood and other organic substances by the influence of pipes, &c., conveying the steam, hot gases, and hot liquids, is by using some good insulating material (non-conductor of heat). This is also desirable from another point of view, in the interests of the manufacturer, namely, in the prevention of waste of the expensive commodity, heat, and thus ensuring a saving of fuel.

For the purposes in view it becomes apparent that these insulating materials will be permanently exposed to the influence of heat, and consequently must be of such a constitution as will enable them to permanently withstand that influence.

It may be remarked at the outset that not every substance that is applied externally to steam pipes and the like is capable of economising heat. On the contrary, certain paints—lead paints—and asphaltum, applied to steam pipes increase the loss of heat therefrom by as much as 25 per cent., the pipes becoming hotter, the radiation of heat more extensive, and the danger correspondingly increased. In fact, an uncovered steam pipe is less dangerous and wasteful of heat than one coated with paint.

Unfortunately, in the trade in insulating materials, just as in the case of boiler fluids and fire extinguishers, a good deal of useless stuff is pushed by advertisement. No consideration is bestowed on the different conditions and fluctuating degrees of heat in different cases, but claims

are put forward that the article will serve for all purposes of insulation, immaterial whether the temperature be  $100^{\circ}\text{C.}$  or  $200^{\circ}\text{C.}$ , and whether or no the material will be exposed to vapours, dust, or moisture.

Credit for having treated this question in a more scientific spirit is due to Mr. C. Pasquay, to whose work on the subject reference may be made.

There is no such thing as a universal insulating material, suitable for pipes of all kinds, unless one disregards expense and selects the best and dearest, even in cases where a cheaper and less efficient article would answer just as well.

At one time, use was made, for this purpose, of mixtures of loam, straw, sawdust, rags, &c., which were also applied in a very primitive manner. The sudden ignition of similar insulating material on a steam engine at Warren (U.S.A.) caused the destruction by fire of a large cotton mill. In this case the material was exposed to a temperature of only  $150^{\circ}\text{C.}$ , but gradually charred and then took fire on slight provocation.

This serious fire caused the attention of interested circles to be drawn to the great danger of so-called insulating materials; recourse was had to others, at first merely to other mixtures, including wood charcoal, loam, hair, syrup, slag, and slag-wool, incorporated into a plastic mass and applied direct. These masses being found wanting in certain particulars, others came into use, viz., cork, cocoanut fibre, cow-hair, clay, asbestos, kieselguhr, lime, gypsum, canvas, &c. The experience gained with these substances indicates that, in order to ensure great economy of heat—leaving the question of fire risk entirely out of consideration—the method in which the insulating material is applied to the steam pipes is more important than the class of material employed. Hitherto, this factor has been comparatively neglected and considered unimportant, but is in reality of the greatest moment, both from an economic point of view and that of fire risk. Only when the method of application and the composition of the material had been duly appreciated as factors of success could the state of affairs in this connection be considered as normal.

From the standpoint of fire risk a number of problems still remained for solution, *e.g.* the behaviour of the insulating material on exposure to heat; the permanence of its resistance to the influence of the latter; behaviour towards moisture, concussion, vibration, and—a point of peculiar importance—flame in the event of an outbreak of fire; finally, the probability of corrosion of the metal pipes by moisture, vapours, or gases absorbed from the air.

For security from fire the question of the behaviour of the material towards flame and sparks is the more important, inasmuch as practical experience has taught that even insulating materials containing 72–74 per cent. of fireproof kieselguhr, have proved capable of spontaneous ignition (and even of taking fire on the approach of a light), after prolonged exposure to a temperature of  $240^{\circ}\text{C.}$  furnished by the steam passing through the protected pipe. The combustion took the form of smouldering, which progressed at the rate of about 40 inches in nine hours.

In selecting an insulating material the chief points to consider are the temperature and velocity of the steam. The usual temperature and pressure of the ordinary steam employed in factories is  $120^{\circ}$ – $200^{\circ}\text{C.}$  and

2–15 atmos. respectively, the superheated steam measuring 200°, 250°, and 350° C.; consequently the limits are somewhat extensive.

The margin of temperature between 120° and 200° C. is a point of special importance in connection with the fire risk, since it comprises a range within which organic substances begin to alter, char, and burn. Even at 120°, 140°, and 160° C. these substances become friable, brittle, decompose, turn brown, and, if the exposure be prolonged, will smoulder and burn (wool, fibres, cork, textiles, &c.).

Vegetable organic substances readily succumb to these temperatures, those of animal origin resisting better owing to their less inflammable character. For instance, experiments have shown that wood-wool, wrapped round a steam pipe containing steam at 15 atmos. pressure and 200° C., is converted, within an hour, into a readily inflammable pyrophoric charcoal. Fortunately, the questions of safety against fire and economising heat are not antagonistic, but may be solved, easily and conjointly, by insulating the non-conducting insulator from the steam pipe.

This may be effected in the following manner: the steam pipe is lapped round with sheet metal, stamped like a grater, so that the projecting tongues formed by the stamping process leave a free air space of about half an inch between the pipe and the metal casing, and at the same time insulate the latter. On this casing is then applied the non-conducting material to prevent radiation of heat, *e.g.* hair-felt, cork, wool, silk, cotton, cocoanut fibre, jute, &c.; and these stuffs are protected from direct contact with the steam pipe, and therefore from the risk of charring, &c., by the stratum of air.

For very hot steam pipes, especially those conveying superheated steam at 200°–350° C., the tips of the metal tongues are directed outward, and over them is laid a second (smooth) sheet of metal for the support of the non-conducting material.

It has been alleged on several sides that a metal jacket is sufficient to prevent radiation of heat, provided it be lapped tight enough, leaving a comparatively large air space next the steam pipe; but practical tests have demonstrated that this method is attended with great drawbacks, and that the air space itself is a source of danger when its dimensions vary much above or below three-fifths of an inch, the maximum benefit being obtained with a space of one-half to three-fifths of an inch, irrespective of the diameter of the steam pipe, since, if made larger, it renders the whole system cumbrous. Again, a simple metal jacket is easily damaged if a ladder be rested against it, or by concussions in the pipes; and any breakage in the jacket allows the heated air to escape, thus not only nullifying the effect of the lagging, but also constituting a source of accident, such, for instance, as explosions caused by the hot air impinging against a petroleum lamp.

The loss of heat from a damaged metal jacket is considerable even in the case of horizontal pipes, but still more so if the pipes are on the slope, and most of all when they are vertical, the loss in the latter event being greater than if the pipe were entirely uncovered.

The question as to which insulating material is the best has been investigated by numerous trials, chiefly by C. Pasquay, the result showing that silk is the best preventive of radiation, whereas hair-felt, wool, cotton, cork, cocoanut fibre, and jute are less economical.

To fully meet all requirements, however, silk lagging requires to be  $\frac{3}{4}$ – $1\frac{1}{2}$  inches thick, according to the temperature of the steam, and must be freed from all vegetable impurities by carbonising. A new insulator for steam of 320° C. and over, known as "Pyrostat," is composed of asbestos (90 per cent.), Glauber salt (8 per cent.), kieselguhr, and dextrin.

Whatever kind of insulating material be employed, it must be protected from all contact or impregnation with fatty or oily substances. The droppings from an oil lamp, for example, may convert the insulating material into a very dangerous substance, on account of its constantly hot condition and susceptibility to spontaneous ignition when greasy. The same result will ensue if the insulated pipe be used to hang greasy clothes or oil rags on.

A bad and readily inflammable insulating material forms the best means of spreading flame to all parts of the works; consequently, all such materials of an inflammable character should be made flameproof, externally at least.

## CHAPTER X

### ELECTRICITY

REGULATIONS for the prevention of accidents in electrical installations have been laid down by various legislative enactments; but as these prescriptions have for the most part been drawn up for the use of experts, and therefore offer no explanation, to the lay reader, of the causes of certain phenomena, it will be necessary to enlarge somewhat on this subject, without, however, treating it exhaustively.

Electricity is the most powerful source of heat known; and this fact must be taken into consideration by every insurance company and every factory owner.

The effect of electricity may be manifested by three different classes of phenomena:—

1. By the incandescence of a wire or metallic object;
2. By the production of sparks (electric, not fire sparks);
3. By the formation of luminous arcs.

Another manifestation, which is not directly visible or tangible, consists in the decomposition of chemical compounds.

In connection with all these phenomena electrical energy may become a source of fire risk, and one can only hear with surprise (so far as it relates to chemico-technical premises) the frequently urged assertion that electric installations are safe as regards fire; for, though it is not beyond the bounds of possibility that the manipulation of electricity *may* be rendered harmless, we are still far from the attainment of this ideal.

For the present we must rest content with the fact that the numerous fires caused by electrical plant are less attributable to electricity, *per se*, than to defective and ignorantly planned installation due to bad materials and careless workmanship—dangerous short-circuiting being quite a notable feature in many works where electric plant is in use—with the result that numerous accidents have to be recorded.

## 1. Electrical Installations

The ordinary public is not in a position to judge whether an installation is properly carried out, and whether the material is good; consequently, when the purchase of electrical plant is in question, the usual tendency is to give the contract to the party making the lowest tender. The result of this practice is that the plant is a constant source of danger from fire, and a risky object of insurance, the danger increasing as time goes on, because this class of plant is very susceptible, liable to alteration, and requires to be not only properly and skilfully constructed, but also well looked after.

In order to minimise the risk of fire in electrical plant, the latter must not merely be constructed in the most perfect manner and of the best materials—and there are plenty of firms of good repute to fulfil this requirement—but all the details of the plant must be adapted to the special character of the works, and finally be maintained in a perfectly safe condition.

A thorough inspection of the electrical plant, which should be performed once a year, is indispensable for the minimising of the fire risk of the establishment. This task should not—as is, unfortunately, too often the case—be entrusted to scientists, teachers, fire brigade officials, opticians, mechanics, or any *soi-disant* expert, unless the person appointed is also a skilled electrician, both in the theoretical and practical branches of the subject, and thoroughly acquainted with the progress of electrical technology up to date, such knowledge being essential to enable any one to judge the degree of safety possessed by an installation.

An expert in low-tension plant should never be appointed to judge high-tension plant, but only one who is accustomed to the latter.

Mention must here be made of another circumstance that may lead to unexpected danger from fire. No factory remains permanently in the same condition, and nowhere are there so many structural alterations, improvements (or the reverse), and extensions as in chemico-technical works. Now, these alterations, necessarily attendant on progress, are a frequent cause of depreciation in initially well-laid electrical plant, especially the conducting wires. As an instance, it sometimes happens that, where an originally excellent electrical plant has had to be enlarged in consequence of other changes in the premises or plant, the final result is found to be highly unsatisfactory and open to all sorts of objections, because the work has been carried out without the assistance of a skilled electrician, and often merely by the works engineer.

In the course of his practice the author has known many such makeshift installations, which not only failed to comply with the provisions of the law, but also presented direct danger of fire.

Electricity in any form may be a source of danger, a glowing wire may be in a position to ignite solid substances, or explode gases and vapours. Both sparks and luminous arcs are equally dangerous, and the last named also furnish particles of glowing carbon, which should be carefully collected wherever readily inflammable substances are in question. Electricity should not be generated in any room containing explosive or inflammable dust and gaseous mixtures, nor should the machinery required for its production or utilisation (dynamoes, &c.) be erected in such spots.

With regard to the danger of electric wires to clothing, see *Clothing*.

Electricity may be generated in almost any class of operations even without the knowledge and against the wishes of the owner of the works. This may result from the friction of waste steam on metallic objects, machinery in motion, driving belts, rubber rollers, metals in intimate contact, metallic powders or dust in course of grinding fibres, wool, glass, resin, resinous substances, rubber (if any of these substances be gently ground or set in motion), gases or vapours escaping with violence from any vessel, *e.g.* liquefied carbon dioxide out of gas cylinders, hydrogen or coal-gas from an air balloon (balloon explosions); see also *Dry Cleaning*.

Ample opportunities also arise for the formation of electric sparks, and where this is the case, means should be devised for the removal of inflammable liquids, gases, vapours, and dust.

The greatest source of danger is short circuiting, for, out of 128 fires known to have originated in electric plant in 1898 and 1899, 63, or nearly 50 per cent., were attributable to this phenomenon, which is described in the following paragraphs.

## 2. Short Circuiting

To utilise the energy of the electric current for lighting power or electrolysis, it must be conveyed through a conductor to a lamp, electro-motor, or a solution of chemical salts. The work done, the current flows away through the return wire, just as steam is conveyed to and from the engine and discharged as waste.

In the same manner as the engine piston offers a resistance that must be overcome by steam, so the lamp, &c., offers a more or less considerable resistance to the passage of the electric current. Consequently, if the current, in passing through the wire, encounters a spot that is defective in any way or imperfectly insulated, and therefore opposes a lower resistance to its escape in an outward direction, it naturally chooses this path which is easier and generally (not always) shorter, in preference to passing through the lamp or other object which it should traverse. Since the line and return wires are often laid close together, the latter is the path mostly chosen by the lazy current. As the current has not performed its task, it is able to exert its undiminished energy in the return wire or other object traversed, and, by reason of its great heat-producing power, raises this object to incandescence, the result being fusion or even combustion of the wire, &c., and an outbreak of fire of a more or less injurious nature, according to the character of the surroundings. This phenomenon, which may proceed in divers ways, is termed "short circuiting."

The several proximate causes of short circuiting are:—

1. Defective insulation of the wires.
2. Damage to the initially good insulation, by
3. Excessive heat, moisture, washing away, friction, defective repairing, or suspending extraneous objects on the wire.
4. Short circuiting may be produced in naked wires by rust, contact with another wire, damp walls or articles, or by too close proximity to another wire of different voltage.
5. Overloading the conductor, and thus causing it to grow red hot, by coupling up too many incandescent lamps in the circuit.

### 6. By lightning.

The best preventives of these dangers are, excellence of installation, insulation, protecting the endangered wires, providing lead safety plugs, and mounting all naked wires away from contact with wood or inflammable materials.

## 3. Applications in Chemistry

So manifold are the uses of electricity in medicine, for lighting, as a source of motive power, in chemistry, and in chemical industries, that it is impossible to recite them all. In chemistry, for instance, it is employed in the recovery and refining of gold, silver, copper, nickel, aluminium, sodium, potassium, phosphorus, carbides, carborundum, alkalis, chlorine, chlorates, bleaching powder, potash, soda, persulphuric acid, and ozone; in electro-plating, in organic chemistry (iodoform); as also in tanning, sugar refining, &c. In many of these industries its employment is not yet perfected, though it gives promise of becoming so. According to Heinzerling the applications may be divided into three main classes:—

I. (a) Continuous current for decomposing water, whereby the oxygen is employed as an oxidising agent, the hydrogen as a reducing agent (organic, colour chemistry).

(b) Continuous current for decomposing metallic salts—

1. Chemical analysis—determination of chemical elements.
2. Metallurgical processes—recovering numerous heavy metals, copper, gold, silver, tin.
3. Electroplating—gilding, silver-plating, copper-plating, nickel-plating.
4. Preparation of chlorates, persulphates, white lead.
5. Bleaching, as in papermaking.
6. Tanning, accelerating the tanning process.

II. Continuous current of low voltage and high amperage acts at high temperatures on fused masses, metallic salts, in the manufacture of potassium, sodium, aluminium, magnesium, rubidium, caesium, and chlorine.

III. Continuous or alternating current.

By the interposition of resistance in the circuit, the energy of the electric current is utilised in the production of extremely high temperatures ( $3000^{\circ}$ – $3500^{\circ}$  C.) in electric furnaces, for fusing metals, preparation of carbides (calcium carbide), carborundum (silicon carbide), phosphorus, also for welding and soldering.

In the first series of operations large volumes of hydrogen are frequently liberated, and this, in admixture with air, furnishes a very explosive gas; whilst in the third series carbon monoxide, which is also combustible and explosive with air, is formed. Hence, on account of the attendant danger, suitable provision must be made for the removal or consumption of these gases by means of ventilators or by burning.

## 4. Accumulators

The term “accumulators” as here used does not refer to the apparatus employed for subjecting liquids to high pressure for the service of hydraulic presses, pumps, cranes, &c., but relates to batteries for the storage of electrical energy.

Although the question of accumulators is sufficiently dealt with in the general regulations relating to electrical installations, it is advisable to discuss the matter in connection with the following particulars.

Loss is always incurred in the generation of energy when the production and consumption do not coincide, especially when the excess of the former is considerable, to prevent which loss it is necessary to provide some means of storing up the surplus.

In gas works this object is accomplished by gasometers, in the case of water power by tanks, reservoirs, &c., whereas no means of storing steam has yet been invented. In the case of electrical energy the task is performed by accumulators, which differ from the vessels used for storing gas and water in that the power is stored in latent energy and not as a finished product. In these accumulators the energy is aroused and rendered active only when occasion arises. Accumulators are therefore comparable to loaded weapons, from the powder of which the propulsive gases and vapours first require to be generated by ignition.

The reader desirous of learning more about the numerous types of electrical accumulators is referred to the special works on this subject. At present our attention will be devoted to describing in a popular manner the somewhat intricate and not yet fully elucidated chemical process that goes on in these apparatus.

An accumulator consists of a number of glass cells, charged with dilute sulphuric acid and containing several sheets or gratings of lead in close proximity to one another, these plates being coated with mixtures of lead compounds (minium, litharge) with sulphuric acid.

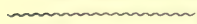
The electric current (charging current) is conducted to the leaden plates, and flows from the one to the other through the dilute sulphuric acid, which is decomposed into anhydrous sulphuric acid and the elements of water (oxygen and hydrogen).

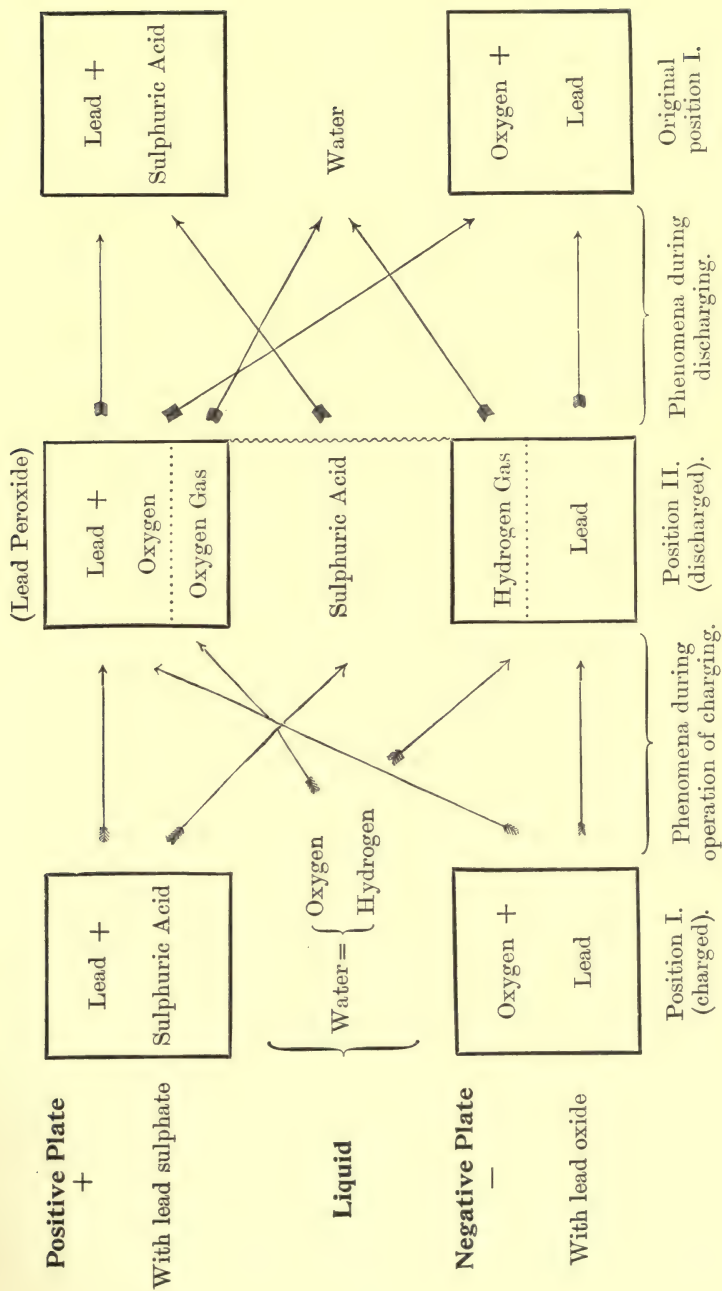
The first plate of the series (the positive plate) contains solid lead sulphate, whilst the final plate (negative), from which the current passes out of the accumulator, contains lead oxide.

During the operation of charging, the decomposition of the water into oxygen and hydrogen is effected within the liquid; at the positive lead plate the solid lead sulphate is decomposed into: sulphuric acid, which passes into the liquid, and lead peroxide, which remains as a brown mass on the plate and absorbs oxygen.

At the negative plate the lead oxide is reduced to a porous mass of lead, in the interstices of which collect the bubbles of hydrogen gas liberated from the water.

When this second reaction is completed (II. on accompanying sketch), the accumulator is charged, *i.e.* the electrical energy supplied by the current has become chemical energy.

On the two extreme plates being connected by a conducting wire , the entire process is reversed, and the discharged current traverses a direction opposite to that taken by the charging current. In this operation the chemical energy is reconverted into electrical energy, and the accumulator discharged, inasmuch as the sulphuric acid returns from the liquid to the positive plate and combines with the lead to form lead sulphate; the gases leave the two plates and unite to form water; and the oxygen from the lead peroxide recombines with the lead in the plates to form lead oxide. In this manner the primary condition of the apparatus is restored, the whole sequence of operations being capable of graphical expression as in the appended diagram.



Accumulators are dangerous on account of the oxyhydrogen gas liberated, and the liability to short-circuiting. These risks may be minimised by efficient ventilation of the apartment; prohibition of entry by unauthorised persons, smoking, or the introduction of naked lights; heating by steam exclusively, lighting with closed lamps only (protected, double bulbs); above all, keeping the conducting wires, frames, and cells dry, since otherwise short-circuiting may occur. The room must be kept locked, and all other kinds of work in accumulator rooms must be strictly prohibited.

# PART III—DANGERS CAUSED BY GASES<sup>1</sup>

## CHAPTER XI

### OXYGEN, OZONE, CARRIERS OF OXYGEN

#### 1. Oxygen

THOUGH not itself combustible, this gas plays the chief part in all cases of combustion, being the foster-parent of all fires and acting as a "chemical bellows" therefor; in fact, without oxygen there would be no fires. This gas is the active constituent of air, so when we speak of a draught that fans the flame, or of the fire going out for lack of air, we refer to the oxygen contained in that air, though it is present therein in only a relatively small proportion, viz., about 20 per cent., the remaining 80 per cent. consisting of incombustible nitrogen, which is fatal to all combustion. Nevertheless, despite the preponderance of this adverse nitrogen and its own dilute condition, it is the oxygen in the atmosphere that, by its presence or absence, decides the question of fire or no fire.

A corresponding influence is exerted by oxygen in explosions. *It* renders gases explosive, since without its presence the latter would burn just as quietly as any other inflammable substance; and *it* alone enables solid substances to explode, by its presence in sufficient quantity chemically combined therein. (To this rule there are certain exceptions, especially among nitrogen compounds.)

For the above reasons, this gas must be dealt with first of all, and a knowledge must be gained of its highly important behaviour in connection with fire risks.

The chief danger of oxygen resides in its capacity for rendering substances combustible, or accelerating their tendency thereto, and of making combustible gases explosive. Since, for the performance of many technical processes, combustibility is a highly desirable property for certain materials to possess, oxygen has become an indispensable adjunct in technology, and its general application has only been delayed by the difficulties and expense of production.

Until very recently the preparation of oxygen was a troublesome and somewhat dangerous operation, being effected by heating certain highly oxygenated compounds, *e.g.* potassium chlorate, manganese dioxide, sodium nitrate, mercuric oxide, potassium chromate, the temperature necessary for the process being 300°–400° C., and, in the case of sodium nitrate,

<sup>1</sup> See also *Gas Explosions*.

600° C. In this operation, unless the heat be applied with care, violent instantaneous liberation of the gas is liable to occur, shattering the vessel and producing serious explosions; again, the heated materials clog together, and prevent the gas from escaping, the consequent accumulation of the gas producing a high pressure inside the vessel, and leading to explosion. The most dangerous substance in this respect is potassium chlorate (see *Chlorates*).

The method of preparation now in use is of an improved character and safer, although some very high temperatures are employed. The principle of the operation is as follows. Heat is applied to a substance which, at high temperatures, absorbs oxygen from the air, and liberates the same again when heated still higher. Such a substance is found in barium oxide (caustic baryta), which, when heated to 500° C. in a system of steel retorts, takes up oxygen from the atmosphere and is converted into barium peroxide. When this conversion is complete, the air supply is cut off, and the temperature is raised to 1000° C., whereupon the peroxide parts with its superfluous oxygen again. When strong pressure is applied, the absorption and disengagement of oxygen is said to occur at 800° C.

The same purpose is served by a mixture of sodium manganate and sodium hydrate, but in this case a temperature of 200° C. is sufficient; lead oxide (changing to lead peroxide) is available for the same end, at 300°–400° C., and cuprous chloride at 200°–400° C.

A more dangerous method is that of preparing oxygen from hydrogen peroxide, which, though it needs only a slight application of heat, is often attended with serious explosions, since the substance itself (*q.v.*) is explosive.

Owing to the property of oxygen of combining with all substances, usually with the accompaniment of a violent outburst of flame, it is natural that all explosions occurring in presence of this element should spread fire; hence no inflammable materials should be present where this gas is used.

The problem of producing oxygen cheaply having been solved, or nearly so, it became necessary to convert the gas into a portable form for technical purposes, its storage in the gaseous state being too inconvenient, and its employment and transport impossible. On this account it was liquefied by exposure to a temperature of  $-119^{\circ}$  C. and a pressure of 50 atmospheres, being then stored and transported in explosion-proof steel cylinders, which come under the same regulations as apply to other liquefied gases. In this case particular stress must be laid on the provision that the oxygen cylinders must not be used for any other gas (and *vice versâ*), even after they have been thoroughly emptied of their contents. They must also be protected from any source of heat, stored in the cool and out of the sun's rays, since heating produces considerable tension.

The uses of oxygen are various, and will become still more extensive as time goes on. At the present time it is employed in the manufacture of varnish, sulphuric acid, and ozone; for lighting, in the oxyhydrogen blowpipe, metallurgy, for soldering metals, blasting, firing boilers, medicinal purposes, disinfection, bleaching, &c.

In admixture with combustible substances (cotton, paper, carbon), *liquefied* oxygen explodes violently when ignited by electricity or by

detonators; but in the absence of violent ignition the mixture merely burns with detonation.

Oxygen must be kept apart from all places where dusty materials are used, or dangerous gases likely to be liberated, since it considerably augments the risk of explosion in either case. Oxygen is particularly dangerous for the following substances: all explosives, fulminates, chlorates, picrates, bronze powders, metallic powders, resins, phosphorus, sulphur, nitric acid, and sulphuretted hydrogen, as well as for all the so-called dangerous liquids, and especially their vapours, the latter acquiring a peculiarly dangerous character when oxygen is present in any proportion.

## 2. Ozone

Ozone is a form of oxygen exhibiting the dangers of the latter in an increased degree. This gas is nothing but oxygen in a more active form, and discharges the same functions in an intensified manner. For this reason it is still more dangerous than oxygen when liquefied by exposure to  $-105^{\circ}\text{C}$ . and a pressure of 125 atmospheres. In fact, mere contact with organic substances or inflammable gases, without ignition, suffices to explode liquefied ozone (see *Spontaneous Explosion*).

All that has been said with regard to oxygen applies also to ozone, only in a stronger degree.

## 3. Carriers of Oxygen

All substances that are chemically highly charged with oxygen or ozone are said to be carriers of oxygen (or ozone).

All these compounds contain a portion of their oxygen in a loosely combined state, and will part with this when a favourable opportunity occurs. Hence, carriers of oxygen behave like this element itself, and exhibit the same dangerous properties.

The majority of oxygen carriers are oxides, which in this event are known as peroxides; but certain acids (*q.v.*) are also supersaturated with oxygen, and these are called per-acids (permanganic acid). The nitrates and chlorates must also be regarded as carriers of oxygen.

When the liberation of oxygen by these compounds is effected in an atmosphere of inflammable gases or vapours, or in direct contact with organic substances, like resins, ethereal oils, or mineral oils, and the temperature is merely slightly elevated, an immediate ignition of these substances may occur, if the circumstances are favourable. Certain carriers of oxygen will ignite organic substances even at the ordinary temperature.

The most important carriers of oxygen, so far as our purpose is concerned, are enumerated below, the temperatures or other conditions at which they liberate the oxygen, and therefore become dangerous, being also mentioned.

Barium peroxide, at  $800^{\circ}\text{C}$ . or  $1000^{\circ}\text{C}$ . (see *Preparation of Oxygen*).

Lead peroxide, when rubbed on any surface along with amorphous phosphorus and with sulphur. It commences to disengage oxygen at  $300^{\circ}\text{C}$ ., and at red heat one-half of the total oxygen is already liberated.

Manganese peroxide, at  $400^{\circ}$ – $500^{\circ}\text{C}$ . or on warming with sulphuric acid.

Potassium peroxide } At white heat, when dissolving in water, and  
Sodium peroxide } also, though gradually, when gently warmed.  
Hydrogen peroxide (see under *Disinfection*).

Perchloric acid, at the slightest opportunity, even during storage, with violent explosion.

Potassium perchlorate, at 400° C.

Pernanganic acid, on gentle warming, any organic matter present being thereby ignited.

Potassium permanganate, in a warmed solution; dry, at 240° C.; when mixed with sulphuric acid, it will ignite all inflammable gases, vapours, ethers, &c. The dry salt tends to ignite spontaneously when suffused with glycerin.

Iodic acid and periodic acid, at 300° C.; at the ordinary temperature in presence of organic matter.

Persulphuric acid, analogous to hydrogen peroxide.

Potassium or ammonium persulphate, at 100° C.; at the ordinary temperature when dissolved in water.

Potassium perselenate liberates oxygen when the solution is warmed.

Chloric acid ignites organic matter on simple contact at ordinary temperature.

Chromic anhydride at 250° C.; detonates and ignites organic substances when suffused with alcohol.

Chlorates (*q.v.*) liberate oxygen in an explosive manner under the influence of friction, shock, concussion, or heat (about 400° C.). When mixed with potassium cyanide, oxygen is immediately disengaged with explosion.

Nitrates (*q.v.*) only begin to liberate oxygen at high temperatures (500°–600° C.).

Nitrogen pentoxide (nitric anhydride), with violence at 50° C.

Nitrous oxide at 500° C.; ignites on contact with incandescent bodies.

Nitric oxide, analogous to the foregoing, but with diminished intensity.

Sulphur heptoxide disengages oxygen very violently during storage, when dissolved in water or warmed.

Bismuth pentoxide (bismuthic anhydride), when heated, or treated with strong acids.

Calcium hypochlorite ("chloride of lime"), when gently warmed or exposed to direct sunlight (see *Lime*).

The following substances may be classed as carriers of oxygen that liberate that element at high temperatures only:—

Ozone, oil of turpentine, colophony (*q.v.*).

Apart from their employment as direct sources of free oxygen for chemico-industrial purposes, the carriers of oxygen are also largely used as disinfectants (see *Disinfection*), for the destruction of organic matter, and in bleaching. For these purposes preference is mainly given to hydrogen peroxide (which is explosive) and sodium peroxide. Bleaching is a term synonymous with the destruction of organic matter and dirt by oxygen (or chlorine).

When sprayed, or in the form of vapour and mixed with dust, carriers of oxygen or ozone augment the danger of explosion by increasing the inflammability, heat of combustion, and explosive power of the dust.

## CHAPTER XII

HYDROGEN GAS, OXYHYDROGEN GAS, AIR  
BALLOONS, CHLORINE AND HYDROGEN1. Hydrogen Gas<sup>1</sup>

Sp. gr. 0.069. Liquefied at  $-234^{\circ}\text{C.}$  and 20 atmos. pressure.  
Explodes at  $555^{\circ}\text{C.}$

THIS is the lightest of all gases, and is readily inflammable and combustible, but not of itself explosive. In respect of fire and explosion dangers, hydrogen is the most important gas and at the same time the most dangerous, since when mixed with air, even in the proportion of only 7 per cent., it forms the explosive oxyhydrogen gas, and retains this property until the proportion reaches 75 per cent. The explosive limit thus occupies a very wide range, and is indeed only surpassed by that of acetylene.

When air is replaced by oxygen, the risk of explosion is still greater, and attains its maximum when the mutual proportion of the gases is 2 of hydrogen to 1 of oxygen, this being the composition of oxyhydrogen gas properly so-called. This mixture can be exploded by the smallest flame or spark, or by heating to  $620^{\circ}$ – $700^{\circ}\text{C.}$ ; when pressure is applied to the gas, explosion occurs as low as  $518^{\circ}\text{C.}$

Both pure hydrogen and mixtures of oxyhydrogen gas can also be exploded by other means, *e.g.* by finely divided platinum (spongy platinum), very finely powdered glass, porcelain dust, or carbon, without the assistance of heat. Of all these substances spongy platinum is the most active in this respect.

When oxyhydrogen mixtures are burned, very high temperatures are developed (over  $2800^{\circ}\text{C.}$  in the case of the pure gas). This heat is utilised for smelting platinum in platinum refineries, the two gases (oxygen and hydrogen) being stored in separate gasometers and fed to the burner of a blow-pipe, where they are consumed, under strong pressure, as soon as mixed. Danger can only arise in these burners in the event of great carelessness.

The mass for lime-sand bricks sets better when the interstitial air has been expelled. If this be effected by an inflammable gas (such as hydrogen), the otherwise fairly safe process may become dangerous; it is therefore advisable to employ some unflammable gas (*e.g.* nitrogen) for this purpose.

Whatever method of preparation is adopted for hydrogen, care should be taken to see that every trace of air has been expelled from the apparatus before the hydrogen gas is ignited, otherwise an explosion will certainly ensue. This precaution should be taken in all cases, especially in the preparation of hydrogen from water, zinc and sulphuric acid;

<sup>1</sup> See also *Oxyhydrogen Gas*.

water and metallic potassium or sodium, or by passing steam over red-hot iron filings at  $800^{\circ}\text{C}$ .<sup>1</sup>

Hydrogen forms the basis of a number of gaseous mixtures extensively employed in lighting and heating on account of their cheapness and heat-producing power. They comprise:—

Oxyhydrogen gas (hydrogen with oxygen, or air);	
Water gas (hydrogen, carbon monoxide, carbon dioxide, nitrogen);	
Power gas (a mixture of water gas and generator gas, <i>q.v.</i> );	
Semi-water gas	} (Mixtures of hydrogen, carbon monoxide, nitrogen).
Mixed gas	
Dowson gas	

## 2. Oxyhydrogen Gas

This gas explodes at  $620^{\circ}$ – $700^{\circ}\text{C}$ ., or at  $518^{\circ}$  (see *Hydrogen*), when under pressure. In the pure state it consists of the elements of water, but only mechanically mixed together, not in chemical combination, viz., about  $33\frac{1}{2}$  per cent. of oxygen, and  $66\frac{1}{2}$  per cent. of hydrogen.

The name is also applied to all mixtures of hydrogen and oxygen; the latter constituent enables the former one to explode. Wherever hydrogen is generated, oxyhydrogen gas is formed, and herein lies the danger of hydrogen, which, though always classed as an explosive gas, is so only in presence of air or oxygen.

Oxyhydrogen gas is used for soldering, fusing platinum, and lighting (as the Drummond limelight). The flame is intensely hot, though very small.

The numerous instances wherein hydrogen or oxyhydrogen gas is generated on contact between metals and water or acids are mentioned under *Metals*. The same gases are also formed during the putrefaction of seeds (under water); in the process of granulating stoneware glaze by pouring the molten mass into a small quantity of water; on the decomposition of water by the electric current; in the electrical purification of waste water and in accumulators (*q.v.*).

In all rooms where large quantities of hydrogen or oxyhydrogen gas are formed, efficient ventilation must be provided to completely remove the gas. This is easily accomplished, the specific lightness of hydrogen causing it to ascend and take full advantage of any ceiling ventilation. In some processes, however, the generation of hydrogen (and concurrent formation of oxyhydrogen gas) is on such a large scale that ordinary ventilation is insufficient for its removal, and the oxyhydrogen gas exhibits altered characteristics which even impart a tendency to spontaneous ignition. This occurs in works where large quantities of metals are dissolved in acids, for the recovery of metallic compounds and salts, immense volumes of hydrogen and oxyhydrogen gas being liberated. The chief examples of this kind are the dissolving of zinc and iron in hydrochloric or sulphuric acid for the preparation of the chlorides or sulphates of the metals in question.

<sup>1</sup> Compounds of metals with hydrogen are called "hydrides," *e.g.* potassium hydride. They are dangerous bodies, the hydrides of potassium and sodium being liable to spontaneous ignition. All the known hydrides liberate oxyhydrogen gas in presence of water, and must therefore be protected from contact with that liquid and its vapour.

Very powerful explosions have latterly occurred in establishments of this kind. Their origin at first seemed problematical, but careful investigation has led to the assumption that the following causes may operate in a factory where zinc chloride is produced by dissolving metallic zinc (chiefly scrap) in hydrochloric acid, the treatment being performed in lead-lined tanks.

(a) *Electric Sparks*.—If, when the tanks are charged with zinc, this metal comes in contact with the leaden lining above the surface of the acid, an electric current is generated; and when this attains sufficient tension it may ignite any oxyhydrogen gas present.

(b) The hydrogen liberated may become mixed with chlorine (from the HCl), in which case an explosion will result directly a ray of sunlight impinges on the mixture.

(c) Old zinc cans may contain fragments of metallic potassium or sodium, which will immediately ignite on contact with the acid.

(d) Small particles of *porous* zinc or rusty fragments of metal are liable to be carried up when the gas is liberated with violence. In such event they behave like spongy platinum, *i.e.* begin to glow in the gaseous atmosphere and ignite the oxyhydrogen gas.

(e) The hydrogen may be given off with such violence that the heat thus generated is sufficient to ignite the oxyhydrogen gas.

(f) When the reaction is so powerful that the gas cannot escape as fast as it is formed, and is therefore exposed to considerable pressure, its explosibility is heightened (*e* and *f* may occur *concurrently*).

(g) Some fragments of the metal may be coloured with lead chromate lacquer, in which event chromic acid may be formed, this then oxidising the lacquer and thereby generating sufficient heat to ignite the oxyhydrogen gas.

(h) The scrap metal may contain traces of gunpowder from cartridges.

Further causes have been mentioned as probable, but chemists have mainly thrown the blame on electricity. To guard against these dangerous explosions it is necessary: (*a*) to keep the work going without interruption, *i.e.* the treatment of the zinc, iron, &c., with acid must not be suspended, whether by night or day, until the whole of the metal is dissolved; which accomplished, an interval of rest may ensue, or the vessels be recharged with fresh metal; (*b*) none of the metal may be allowed to protrude above the surface of the acid, especially any metal in contact with the leaden lining of the tank; (*c*) the lead-lining must be connected with a grounded metallic conductor, so that any electricity generated may be drawn off immediately and prevented from attaining any high tension; (*d*) the charge of metal must be introduced into the acid in such a manner that no air is retained in the cavities; (*e*) the metal must be cleaned of all lacquer and paint before immersion in the acid; (*f*) the dissolving tanks must be fitted with efficient water seals to prevent access of air, and with suitable means for drawing off the liberated gases so that the latter cannot accumulate under pressure. The most important condition of all is that mentioned under (*c*).

### 3. Balloons

A similar phenomenon is the explosion of aeronautical balloons filled with hydrogen. True, the question is not yet finally settled, but so

much is certain, namely, that balloons have suddenly exploded while being emptied of their hydrogen, though kept away from any fire or other source of ignition. It is assumed that the fibrous material in the envelope of the balloon, which is often impregnated with resinous substances to make it waterproof, coupled with the friction of the gas escaping through the metal valve, and the high pressure not infrequently applied in order to accelerate the emptying of the balloon, produce electrical excitation, culminating (when the accumulated electricity has attained a certain tension) in a small spark, which is sufficient to ignite the oxyhydrogen gas formed around the discharge valve.

#### 4. Hydrogen and Chlorine

Oxygen is not always indispensable for the occurrence of hydrogen explosions, since the latter gas when mixed with an equal volume of chlorine (*q.v.*), furnishes a gas that explodes with violence when exposed to direct sunlight—a similar effect also ensuing with artificial, electric, and magnesium light.

The above mixture is still more explosive than oxyhydrogen gas. Owing to its dangerous character it is seldom employed in practice, but it is occasionally formed, unintentionally, in various processes, *e.g.* in the electrolytic production of hypochlorites from bleaching powder, in the electrolysis of chlorine compounds, or of hydrochloric acid, in which latter eventuality hydrogen and chlorine are liberated in equal proportions.

The fact that these processes are not invariably attended by explosions is due to the circumstance that the component gases of the mixture are usually disengaged in unequal proportions, whereas, for an explosion to occur, it is essential that the mixture should consist of equal volumes of each (see *Oxyhydrogen Gas* and *Preparation of Zinc Chloride*).

### CHAPTER XIII

#### INDUSTRIAL POWER GASES

##### 1. Water Gas (Power Gas, Heating Gas)

In treating of this gas it is necessary to briefly consider the several varieties of power or heating gas.

When:—	There results a gaseous mixture of about:—
1. <b>Air or Carbon Dioxide</b> } is passed over glowing coal, <i>or</i>	Carbon monoxide . 30 per cent. } Generator gas (Sulphur gas).
<b>Coal</b> is burned in a deficient supply of air.	Nitrogen . . 70 „ } Hydrogen . . (Little)
2. <b>Steam</b> at 1000°–1200° is passed over glowing coal.	Carbon monoxide . 40 per cent. } Hydrogen . . 50 „ } Water gas. Nitrogen . . 6 „ } Carbon dioxide . 4 „ }

3. <b>Air and Steam</b> }	are passed simultaneously over glowing coal.	Carbon monoxide Hydrogen Nitrogen	} Dowson gas (Mixed gas, Semi-gas).
4. <b>Air</b> at 1000°–1200° C. is passed over glowing coal, and followed by <b>Steam</b> until the temperature falls below 1000° C.		Generator gas and Water gas	

} Power-heating gas.

The processes enumerated above are modified in various ways according to the peculiarities of different installations, and the gaseous products are known by various names—water gas, for instance, being often called power gas, whilst generator gas is termed heating gas, and so on.

The object of all these processes is to convert the constituents of the solid and liquid raw materials (coal and water) into the gaseous state and then utilise the gas for heating, power, or lighting, *i.e.* to employ gaseous fuel in place of solid.

Water gas has the sp. gr. 0.540, burns with a flame temperature of 2831° C., is colourless, inodorous, readily inflammable, and less explosive than hydrogen, owing to the presence of incombustible admixtures (nitrogen and carbon dioxide).

The explosive limit of mixtures of water gas and air begins when the percentage of the latter reaches 9 per cent., and ends at 55 per cent. In the case of hydrogen the limits are 7 and 75 per cent. respectively, and therefore wider.

With 9–14 per cent. of water gas, the explosions are very faint and merely detonative flashes; between 14 and 18 per cent. the flashes are accompanied by an audible report, and the maximum explosive force is exerted from 18 to 31 per cent., from which point onward it decreases till 55 per cent. is reached, whereupon it disappears. With hydrogen the maximum of explosibility occurs at 14–23 per cent.

Though less dangerous taken altogether, water gas has a higher velocity of explosion than other gases, and the velocity of the explosion wave is far more rapid, the explosion more violent and forcible, than is the case with many other gases, coal gas in particular.

Water gas is also inodorous, and even a quantity attaining the explosion limit may be present without the same becoming apparent by the smell. This constitutes a grave danger, which can only be obviated by an addition of some strong-smelling substance, such as mercaptan.

The chief employment of water gas is in the production of intense heat for welding, soldering, and heating. It is also used for lighting, though devoid of illuminating power. It is even not improbable that, by reason of its low cost, easy preparation, and heating power, it may ultimately displace coal gas.

For lighting purposes, water gas is carburetted (see *Carburetting*) and is then very efficient; where, however, incandescent mantles are used, carburetting is entirely needless.

The appliances for making water gas include: boiler, generator, scrubber, motor, gasometer, and (if the gas is to be used as an illuminant)

purifier. In the latter event a carburettor must be added, unless mantles are used.

The generator consists of a shaft furnace charged to a depth of 3–10 feet with the fuel to be gasified (coke, wood charcoal, anthracite, or, more rarely, coal). The fuel is kindled from below and air is blown in until the glowing mass reaches 1000°–1200° C. (see *Carbon Monoxide*). The resulting gas is termed generator gas and consists chiefly of carbon monoxide and nitrogen, with a little hydrogen. When this temperature is reached, the air-blast is stopped and replaced by a current of steam, which may in some cases be superheated. This treatment furnishes the true water gas: a mixture of about 40 per cent. carbon monoxide, 50 per cent. hydrogen, and 10 per cent. of carbon dioxide and nitrogen. Generator gas and water gas together form power gas. While the gas is being produced, the temperature sinks to below 1000° C., whereupon the formation of carbon monoxide is suspended, and the undesirable dioxide is produced; to obviate this, the steam is turned off and the air-blast started afresh, whereby the temperature is again raised to 1000°–1200° C.

The process is therefore an intermittent one, and consists of alternate periods of blowing up and gas formation, the former lasting about 10–15 minutes, and the latter 2–6 minutes. In some works, however, the blowing up takes only 3–4 minutes, whilst the gas producing lasts for 12–17 minutes.

Owing to the numerous alterations in the course of a day, a considerable danger accrues when the plant is not kept perfectly air-tight. The greatest danger arises from the air finding its way into the generator, and thus forming an explosive gaseous mixture, at starting and stopping.

In these and similar installations for gas making, numerous precautions must be observed.

The coal used must be of good quality and poor in gas, since, in the case of bituminous coal, particles of the same, containing hydrocarbons, may be carried away in a glowing state by the chimney draught.

Any leakiness in the damper must be repaired as soon as detected; no pipe joints should be allowed in the enclosed portions of the furnace; all conduits must be as short as possible. The number of taps must be reduced to a minimum, and each must be fitted with a key to prevent tampering by unauthorised persons.

All the pipes must be tested for leaks by the Muchall tester, which must be set up at the front end of the same.

Where the gas is inodorous it must be treated to an addition of mercaptan, by passing the gas through a 5–10 per cent. alcoholic solution of that substance.

The first gas produced in blowing the plant, or after the apparatus has been standing still for more than twenty-four hours, must be discharged into the open air.

After a long period of idleness, all parts of the apparatus must be cleared out by two lots of fresh gas, which must then be discharged into the open; then, and then only, may the (air-free) gas produced in the plant be used.

Before repairing any part of the plant, the same must be sweetened by a thorough draught of air; otherwise the small traces of gas left behind may produce great damage when soldering is being done or the interior of the apparatus is being inspected with open lights.

Naked flame should be avoided as a test for leakage, soap solution being the sole permissible test.

The feed-aperture cover of the generator should be fitted with a cooling device, to prevent it from being warped by the heat, and thus rendered leaky.

When water gas is employed in admixture with air, for welding, &c., the gas-burner slits must be very narrow, and a layer of fine wire gauze must be inserted in the gas pipe, to prevent the flame lighting back and causing an explosion. The pipes must also be fitted with a safety valve, opening under a gas pressure of about 38 inches water gauge.

Where the pipes bend at an angle, the end of the pipe must be closed by an elastic rubber cap, which bursts in the event of an explosion in the pipe, and thus prevents any extension of the explosion.

All rooms where use is made of water gas, or similar gases, must be provided with ventilation in the roof, the gas being lighter than air on account of its hydrogen content. These rooms must be subjected to the same conditions as those prescribed for rooms wherein dangerous gases are produced.

## 2. Dowson Gas

In the case of Dowson gas, semi-gas, mixed gas, no addition of mercaptan or the like is required, the gas smelling strongly enough, except when their smell has been eliminated by the method of purification adopted.

Such gases, when used for heating (*q.v.*) may play a twofold part:

Simple gas firing, as in the case of boilers, gas furnaces, kilns for burning cement, porcelain, bricks, or clay. The main point here is to secure the utilisation of the full extent of the flame and the amount of heat furnished by the burning gas.

Regenerative gas firing is employed in glass furnaces, foundries, and metallurgical processes, where the main consideration is to utilise the maximum heat of combustion.

In both methods the gas is mixed with hot air in the combustion chamber; but in regenerative firing, use is also made of regenerators, usually mounted in pairs, for heating the gas and air by means of the hot waste gases of combustion escaping from the combustion chamber.

These hot gases raise the regenerators to a very high temperature, whereupon the gas and the air of combustion are introduced, and, when a high temperature has been attained, are conveyed to the combustion chamber. Meanwhile the hot waste gases have been diverted to the second regenerator, so that the heating and cooling of these chambers proceeds alternately.

Fireproof materials must be used throughout in the construction of this class of plant, the temperatures ranging between 800° and 2000° C.

The newly introduced Mond gas (so-called after its inventor) presents a contrast to Dowson gas in being prepared from cheap, bituminous coal, instead of from the dearer, less gassy coals. In the Mond process the difficulties hitherto arising in the use of bituminous coal, viz., frequent obstruction of the generators, and an abundant deposition of tar, are obviated by consuming the tar vapours in the furnace, and by gasifying the bituminous coal at a low temperature—an object accomplished by the introduction of large volumes of steam.

The Mond gas generated in a firebrick producer, holding a charge of about half a ton, contains  $2\frac{1}{2}$  per cent. of methane, 26.4 per cent. of hydrogen, and 10 per cent. of carbon monoxide, the remainder consisting of carbon dioxide and nitrogen. According to the coal used, the sp. gr. is 0.987–1.015. The maximum temperature attained during the process is  $450^{\circ}\text{C}$ .

## CHAPTER XIV

### CHLORINE

Density 2.45.

CHLORINE liquefies at  $-35^{\circ}\text{C}$ ., or at zero and 6 atmos. pressure, and solidifies at  $-102^{\circ}\text{C}$ . It is incombustible, but, like oxygen, is capable of supporting the combustion of certain substances, and of forming highly dangerous compounds with several elements.

Mixed with hydrogen in equal parts, or with acetylene, it explodes in sunlight. Paper, textiles, fibres, and porous combustible materials, which have been soaked in oil of turpentine, resin, or ethereal oils, will ignite spontaneously when plunged into chlorine gas.

The following substances also burn spontaneously in an atmosphere of chlorine: sodium, potassium, phosphorus, bismuth, antimony, arsenic, gold leaf, brass bronze, copper bronze, gold, platinum, iron (at low red heat), and acetylene gas.

Chlorine combines with nitrogen to form the highly explosive nitrogen chloride (*q.v.*), which is prepared by passing chlorine through ammonia or ammoniacal liquids.

With oxygen it combines to form the highly explosive chlorates, inflammable chloric acid, or explosive perchloric acid. With ethyl it forms ethyl chloride, boiling at  $12.5^{\circ}\text{C}$ . and readily inflammable; with methyl the combustible methyl chloride. Both compounds are prepared by passing chlorine through ethyl alcohol or boiling wood spirit respectively. For the behaviour of chlorine towards acetylene, see this latter gas.

The usual method of preparing chlorine is harmless; when hydrochloric acid, cupric chloride, and atmospheric oxygen are employed, a temperature of  $400^{\circ}\text{C}$ . is required. In all cases care must be taken to keep the apparatus from cooling down to such an extent that solid chlorine hydrate is produced, this substance tending to stop up the tubes, and, when warmed, decomposes suddenly, accompanied by an explosion, owing to the instantaneous liberation of chlorine gas (chlorine explosion). Since, owing to the injurious character of chlorine, the producing apparatus is preferably set up out of doors, the possibility of chlorine explosions in the winter is not precluded. Consequently the apparatus should be protected from frost, especially when not in use.

## CHAPTER XV

## AMMONIA

AMMONIA (ammonium hydroxide, *liquor ammoniae*) has the density 0.590, the sp. gr. of the liquid form (solution) being 0.624. At  $-40^{\circ}$  C., or under a pressure of  $6\frac{1}{2}$  atmos., the gas liquefies.

It is erroneous to speak of this gas as inflammable, as is sometimes done. It is, however, combustible in oxygen, with which latter it even forms explosive mixtures. The gas is decomposed by an electric spark, contact with molten potassium, or by passing it through red-hot pipes, explosive hydrogen being liberated. Its most dangerous product, nitrogen chloride, is that formed when chlorine is passed through a solution of the gas. An equally dangerous operation is that of suffusing iodine with ammonia solution, the explosive nitrogen iodide being formed. These reactions, though rare in manufacturing operations, are frequently performed in the laboratory.

Liquefied ammonia is dangerous on account of the high pressure developed on the application of gentle heat, rising from 4.4 atmos. at zero C. to 10 atmos. at  $28^{\circ}$  C. The steel cylinders, in addition to fulfilling the usual conditions prescribed for such receptacles, must be kept cool, and never exposed to the sun or to heat.

Explosions of ammonia gas are never the direct cause of fires, this gas being a very good extinguisher.

Ammonia is produced in gas works (*q.v.*), and also by carbonising organic substances with quick lime (*q.v.*), the usual dangers attending such carbonising plant being incurred by spontaneous ignition of the partly carbonised materials, and formation of explosive gases.

Both ammonia gas and ammonia salts are very good for preventing the spread of flame (see *Antipyrène*).

A peculiar property is exhibited by sulphate of ammonia, or the ammonia liquor from gas works, namely, that if straw, foliage, or similar substances be frequently immersed in or sprinkled with this liquor, spontaneous heating ensues, the temperature even attaining  $100^{\circ}$  C., and if the substances mentioned be piled in large heaps they may grow so hot as to finally take fire.

In connection with fire risk, the following ammonia compounds are also worthy of mention :—

Ammonium cyanide, which volatilises at  $36^{\circ}$  C., and is inflammable.

Ammonium nitrate, which explodes by percussion or at  $70^{\circ}$  C.

Ammonium nitrate detonates on contact with glowing coal, and furnishes nitrous oxide (*q.v.*) when heated.

With ammonia must also be classed hydroxylamine, which is in the form of needles that melt at  $33^{\circ}$  C., and boil at  $58^{\circ}$  C. It is inflammable, and burns briskly in air; on distillation, it explodes when the temperature exceeds  $100^{\circ}$  C., and the distillate must therefore be very thoroughly cooled. In general this substance is very unstable, and it is only at a temperature below  $15^{\circ}$  C. that it can be stored without decomposition.

## CHAPTER XVI

## CARBON MONOXIDE AND ITS COMPOUNDS

## 1. Carbon Monoxide

Density 0.967; explodes at  $636^{\circ}$ – $814^{\circ}$  C.; and liquefies at  $-140^{\circ}$  C. and 35 atmos. pressure.

WHEN coal is burned, two gases may be formed, the harmless carbon dioxide and the combustible carbon monoxide which forms an explosive mixture with air. The predominance of the one or the other of these gases is determined by the temperature prevailing during combustion (see *Power Gas*).

	The Production of Carbon Dioxide.	Carbon Monoxide.
At $375^{\circ}$ C. . .	small	nil
„ $401^{\circ}$ C. . .	somewhat larger	small
Up to $800^{\circ}$ C. . .	about 18 per cent.	about 6 per cent.
„ $900^{\circ}$ C. . .	„ 10 „	„ 16 „
At $950^{\circ}$ C. . .	„ 0.5 „	„ 31 „
„ $1000^{\circ}$ – $1100^{\circ}$ C.	nil	„ 34 „

In all works where organic substances, coal, bones, &c., are carbonised, *e.g.* bone-black factories, ferrocyanide, and ferricyanide works, power gas works, coke-ovens, limekilns, &c., the danger of carbon monoxide explosions first arises when the furnace temperature attains  $900^{\circ}$  C.

A large quantity of carbon monoxide is furnished by charcoal stoves (see *Heating*).

The danger of such explosions is less in works when the production of carbon dioxide alone is desired, *e.g.* limekilns, in sugar works, charcoal burning plant (chiefly producing wood spirit and pyrophoric carbon), ferricyanide works, and bone-black factories, than in those where a preponderance of carbon monoxide is aimed at, gas works, plant for generating water gas, power gas, or heating gas, and blast-furnace plant.

Carbon monoxide is also furnished by glowing coal when the air supply (oxygen) is deficient, or when the carbon dioxide already formed passes over glowing coal at a temperature of about  $1300^{\circ}$  C., or steam is passed through glowing coal at a temperature exceeding  $1000^{\circ}$  C. Large quantities of the gas are also produced in electric furnaces. In presence of air the explosive tendency and force of carbon monoxide are low (hence the comparative harmlessness of blast-furnace gas rich in this oxide), but they may become considerable when the air is replaced by pure oxygen, the risk being still further augmented by the presence of steam or moisture. Where carbon monoxide is produced or used, carriers of oxygen must therefore be excluded, and this gas must never be mixed with oxygen in presence of a naked light. The greater precaution is necessary on account of the absence of any smell that would reveal the presence of this gas.

Mixtures of air and carbon monoxide become explosive when the proportion of the latter attains 13 per cent. and remain so until 75 per cent. is reached; beyond the latter limit the mixture merely flashes when ignited.

## 2. Carbon Monoxide Compounds

With sulphur, carbon monoxide forms carbon oxysulphide, which furnishes an explosive mixture with air or oxygen. This compound is ignited by a spark or flame, and liberates combustible sulphuretted hydrogen when treated with water or alkalis.

Carbon monoxide combines with nickel to form a liquid, boiling at 43° C., and exploding at 60° C.

In the electric furnace, carbon monoxide combines with potassium, forming the explosive compound potassium carbon monoxide.

## CHAPTER XVII

### SULPHURETTED HYDROGEN

Density 1.192; liquefies at 15 atmos. and 10° C.

Of all combustible gases this is the least dangerous. It is easily detected by its putrescent smell, which facilitates the prevention of explosions. Furthermore, the gas is unstable and quickly decomposes in contact with air.

One of the dangers of sulphuretted hydrogen arises from the frequency of its occurrence. Wherever putrefaction is going on (pits, cesspools, sewers), wherever metallic sulphides or sulphurous materials are treated, lignite quenched, soda residues or calcium sulphide residues stored or worked, and wherever sulphur springs occur, there will this gas appear, often quite unexpectedly. Its occurrence in laboratories and factories is also no rarity.

The method of preparing sulphuretted hydrogen by treating iron sulphide with sulphuric acid is not dangerous, provided there are no open lights about; but in the preparation from paraffin and sulphur, the gas may be liberated in an explosive manner.

Explosive mixtures are formed with air, but the reaction is more a flash than an explosion, though when oxygen replaces air in these mixtures the danger is increased. Both the gas and its mixtures are readily ignited by flame or slightly glowing bodies.

Sulphuretted hydrogen should not be brought into contact with fuming nitric acid, carriers of oxygen, metallic dust, bronze powders, or blasting materials containing these substances, since spontaneous ignition may result, apart from the risk of explosion.

Any sulphuretted hydrogen formed in factories should be carefully stored, or else rendered innocuous by combustion.

Seleniuretted hydrogen and telluretted hydrogen resemble the foregoing, and are both combustible.

## CHAPTER XVIII

## NITRIC OXIDE, NITROUS OXIDE

BOTH nitric and nitrous oxide are compounds of nitrogen and oxygen, the first-named containing the larger proportion of oxygen.

Properties.	Nitric Oxide.	Nitrous Oxide.
Density . . . .	1·039	1·527
Liquefies at . . . .	- 93·5° C. and 71 atmos.	0° C. and 36 atmos.
Combustibility . . . .	nil	nil
Hydrogen gives . . . .	inexplosive mixtures	explosive mixtures

Both gases support combustion, and glowing bodies will burst into flame on immersion in either of them. They resemble oxygen in their behaviour, and the remarks made with regard to oxygen also apply to these two oxides, which play the part of weak carriers of that substance. Of the two, nitric oxide parts less readily with its oxygen and is a less active supporter of combustion than the other.

The method of preparing nitric oxide is harmless, copper being dissolved in nitric acid. On the other hand, the recovery of nitrous oxide, by heating ammonium nitrate, is a less easy operation, overheating being liable to result in explosion. The same consequences may ensue if the heating process be continued until the whole of the material is decomposed, and it is therefore necessary to leave off before that point is reached. The danger is less when ammonium nitrate is replaced by a mixture of well-dried potassium nitrate and ammonium sulphate.

Although the danger is not a serious one, it is referred to because nitrous oxide (laughing gas) is frequently prepared by dentists who use it as a substitute for chloroform. Hence, the rooms where it is prepared and used are liable to the dangers inherent in the gas and its uses.

## CHAPTER XIX

## SUBTERRANEAN GASES

### 1. Methane (Methyl Hydride, Carburetted Hydrogen, Marsh Gas, Firedamp).

Density 0·559. Explodes at 656°–678° C. Liquefies at - 82° C. and 55 atmos. pressure.

METHANE is an inflammable gas, which, though not directly used industrially, must be mentioned here on account of its frequent appearance in unexpected places.

It is met with: in bins containing putrefying seeds; pits where

agricultural products are decaying under water; in coalpits, where it constitutes firedamp; in pits with a peaty subsoil; in damp marshy channels or places; coal bins (bunkers) where it is exhaled by the coal; in coal vessels; underneath houses or other buildings, the subsoil of which is connected with marshy ground by channels, conduits, or drain-pipes; and in the decaying mud of ponds, where it ascends to the surface when the bottom is stirred.

All buildings in the vicinity of marshes, marshy ponds or spots, channels or pits, are liable to the danger of methane explosions, more particularly at the end of summer, towards autumn.

The accumulation of methane in cellars and arches cannot be detected by the sense of smell, the gas being almost inodorous; it may also be inhaled for some time without any ill effects.

Sundry paradoxical explosions in underground chambers must be set down to the account of marsh gas.

Methane also occurs in crude petroleum, and likewise in coal gas to the extent of 30-40 per cent. The carbides of aluminium, beryllium, cerium, lanthanum, yttrium, thorium, manganese, and uranium, all furnish methane on contact with water.

In itself methane is not explosive, and it is only when heated to  $656^{\circ}$ - $678^{\circ}$  C., or mixed with air or oxygen, that it furnishes mixtures which explode with violence on contact with flame. When mixed with chlorine, it is exploded by the action of the sun's rays.

Air becomes explosive when the proportion of methane reaches 5 per cent., but ceases to be so when 16 per cent. is exceeded, a mere flashing being then produced. The maximum explosibility is between the limits of 9 and 10 per cent. of methane, this mixture containing just sufficient oxygen for the complete combustion of the methane. The following table shows the explosibility of different mixtures of air and marsh gas:—

Percentage of Methane.	Explosibility.
1-4	nil.
4-6	slight.
6-9	powerful.
9-10	very powerful.
11-13	powerful.
13-16	slight.
above 16	flashing merely.

The presence of 6-7 per cent. of "firedamp" is insufficient to render air explosive, since this gas contains carbon dioxide, which retards explosion and merely permits a slight flashing, but if in addition the air contains finely divided coal dust, then the possibility of a violent explosion is afforded.

Ignition is necessary for explosion to occur. Pure methane is not readily inflammable, and must first be raised to a fairly high temperature. For this reason safety lamps can be very successfully used when it is a question of entering rooms filled with methane.

The low tendency to ignite is counteracted, however, by the high explosibility of the gas when mixed with dust. In presence of floating dust, 3 per cent. of methane is sufficient to render the mixture explosive

(see *Dust Explosions*), and, in this case, the explosive limit does not terminate at 16 per cent.

Methane is still more dangerous when mixed with pure oxygen.

## 2. Ethane (Dimethyl).

Density 1.036. Explodes at 605°–622° C. Liquefies at 4° C. and 46 atmos. pressure.

In contrast to methane, this is a readily inflammable gas, which occurs in petroleum and makes the vapours of same very liable to take fire, especially those from the crude oil. It also occurs in the gases exhaled by coal.

Ethane has no industrial application. When prepared by heating acetylene to 500° C., it is a source of great danger from explosion, and the same applies when the part of heat in this reaction is played by spongy platinum.

## 3. Propane

Density 1.520. Explodes at 545°–548° C.

Also occurs in crude petroleum, and resembles ethane.

## 4. Ethylene (Olefiant Gas, Heavy Hydrocarbon, Elayl, Vinyl Hydride, Dutch Liquid).

Density 0.967. Explodes at 577°–599° C. Liquefies at –1° C. and 42.5 atmos. pressure.

Ethylene is a frequent companion of methane, which it resembles. It forms an explosive mixture with air when present therein to the extent of 4–22 per cent., the maximum effect being produced with 6.3 per cent. It is very highly explosive in association with oxygen, especially when the latter forms three-fourths of the mixture.

It is readily inflammable and combustible; with twice its own volume of chlorine it forms a mixture that lights on exposure to the sun. Recently ethylene has been cheaply and easily prepared (like carbide) from blast furnace slag, the latter being converted into "carbolite" by heating in a powerful electric furnace along with carbon. This product is similar to carbide, and, like the latter, furnishes with water a gas (ethylene) that seems likely to rival acetylene.

# CHAPTER XX

## COAL GAS, GAS PURIFIERS, FAT AND OIL GAS

### 1. Coal Gas

Density 0.4–0.6. Explodes at 647°–649° C. Flame temperature about 1400° C.

LIGHTING gas is a mixture of various gases and vapours (28–35), obtained by heating coal (coal gas) at 900°–1000° C., or fat (oil gas, fat gas) at

600°–800° C. According to the class of coal, the yield of gas varies between 390 and 740 cubic feet per cwt., whilst the same quantity of fat furnishes up to 1130 cubic feet of gas, which can be purified in a less troublesome manner than coal gas.

The dry distillation of coal furnishes, as decomposition products:—

1. **Ammonia water**, containing sulphate and carbonate of ammonia, and ammonium sulphocyanide.

2. **Tar water** (for the constituents, see *Tar*).

3. **Coal gas**, containing:—

(a) Impurities: ammonia, carbon dioxide, cyanogen, sulphuretted hydrogen, nitrogen, carbon disulphide;

(b) Combustible matters (light supporting): hydrogen, methane, carbon monoxide;

(c) Illuminating constituents (light giving): acetylene, ethylene, butylene, propylene, benzol, naphthalene, butyl, and propyl.

4. **Coke**: carbon, mineral matters.

Gas making is an apparently dangerous process owing to the high temperatures employed, the handling of an inflammable gas that passes through a troublesome purifying process, with that very dangerous material, tar, as a waste product, and with the numerous furnaces involved. Nevertheless, practical experience has shown that the business is a very safe one, and that most of the fires and explosions have occurred, not in the gas works, but at the various centres of consumption, and therefore generally some distance from the gas works.

The only explanation of this safety is to be sought in the excellence of the plant, good management, and in the relatively low danger of the coal gas itself when properly handled.

Even the storage of many hundred thousand cubic feet of gas is free from danger. Should the gas in the gasometers be set alight, it burns away quietly, owing to lack of the oxygen necessary to produce an explosion. (The failure for this reason of the attempt made by dynamitards to blow up a large gasometer at Glasgow, several years back, may be remembered.) Greater danger is incurred at the stage when the gas is passing through the purifiers, owing to its impure condition at that point.

Gas works must naturally adopt all the precautions prescribed for dangerous trades, special care being bestowed on the still glowing coke and on the purifying materials. To prevent the wasteful decomposition of gas in the retorts, Lewes recommends that an addition of water gas should be given. However, as this addition must be made during the producing stage, it would increase the dangers of the process.

## 2. Gas-purifying Materials

The materials employed for purifying coal gas consist of a variety of substances, frequently compounds of iron or lime, occasionally in admixture with organic matter (sawdust). When spent, these materials were formerly thrown away, but are now treated for the recovery of sulphur, Berlin blue, cyanogen, and sulphocyanide compounds.

Their chemical composition readily undergoes alteration, and as much as 30 per cent. of sulphur is often present. This instability is a source of danger, since, if the spent matter be piled up in heaps, it easily attains

a temperature of  $60^{\circ}\text{C}$ ., which dries the mass and prepares it for spontaneous heating of a more dangerous character, if the wetting of the heaps be omitted. Sometimes these heaps have been found to have heated to  $420^{\circ}\text{C}$ ., at which temperature both the sulphur and the unstable and readily oxidisable sulphur compounds present (calcium sulphide, iron sulphide) could take fire without difficulty. If the mass contain organic matter, such as sawdust, wood wool, or peat, it will take fire still more readily.

The spent purifying mass must be stored in such a manner as to be fireproof, the heaps being not more than 12 inches deep in order to enable the superficial radiation to nullify the internal heating. At times these masses also liberate large quantities of sulphuretted hydrogen, which is inflammable.

The sulphur is sometimes extracted by means of carbon disulphide (*q.v.*), a very dangerous operation.

Precautions for preventing the risk of spontaneous ignition are adopted in gas works, because if the heaps are allowed to get too hot the quality of the material is depreciated.

Of itself, coal gas is one of the least dangerous of all; the explosion risk, however, may be considerably heightened by the presence of dust from wood, flour, coal, soot, &c.

This gas ignites readily at a flame, but not so easily by contact with glowing bodies; in fact, the temperature of these must be higher than that of slightly glowing iron. Whilst small sparks of intensely high temperature easily ignite gas, this cannot be effected by a large mass of glowing iron at a temperature of  $500^{\circ}$ – $600^{\circ}\text{C}$ . The decisive factor here is the intensity, not the amount, of the heat, and hence electric sparks are more dangerous to coal gas than large masses of faintly glowing metal. Danger from electric sparks is very liable to arise in the case of balloons charged with coal gas (see *Oxyhydrogen Gas*).

Coal gas exhibits a highly characteristic behaviour towards spongy platinum, the latter glowing without, however, igniting the gas; but if the spongy platinum be connected with a platinum wire, which is gradually raised to incandescence by the heat disengaged by the former, the gas will ignite at the glowing wire. This phenomenon is the basis of the numerous automatic gas lighters now sold.

Coal gas is explosive only when mixed with air or oxygen; but, in comparison with hydrogen, acetylene, carbon monoxide, and water gas, the range of explosive limit is very small. Thus:—

A mixture of air with			
4	per cent.	of coal gas	is unflammable.
5	"	"	gives a barely visible flame.
6	"	"	burns slowly.
8–12	"	"	burns quickly with a hissing noise
13–14	"	"	burns in an explosive manner
14–19	"	"	explodes
19–23	"	"	explodes violently
23–25	"	"	burns quickly.
25–28	"	"	burns away slowly.
above 28	"	"	simply flashes.

} Explosive  
limit.

The explosive limit therefore extends from 8 to 23 per cent.; but, should a little dust be present, rapid ignition ensues, even with 3 per cent. of gas, and a violent explosion occurs with 8 per cent. of gas.

The fact that ordinary gas explosions in dwelling-houses and shop windows do comparatively little damage is due to the circumstance that the area of the initial explosion is not sharply defined, the ready inflammability of the gas enabling it to burn away rapidly; moreover, the burner orifices are so small that only a little gas can escape should the tap be accidentally left turned on. Thus, for the air of a room of moderate dimensions (1800–2000 cubic feet) to become charged with merely 8 per cent. of gas, it is necessary for a 7-foot burner to remain open for 20 hours; and then, in the most favourable case, merely a rapid burning, with a hissing noise, will ensue. It is probably seldom that a gas burner could remain on for such a long time unnoticed, since even so small a quantity as 0.3–0.5 per cent. of the gas can be detected by its smell. In the event of a large fracture of the pipes, the danger is, of course, greater, but at the same time becomes more readily apparent.

The danger of gas explosions is diminished by yet another circumstance: coal gas, being very light, tends to ascend, and therefore is more readily dissipated than heavy gases that hang about near the floor, whence they are dislodged with difficulty. For this reason it is harder for the gas to accumulate in sufficient quantity to produce an explosion, and it is highly probable that this scarcity has weakened the force of many gas explosions. If the gas had been heavier than air it would have been far more dangerous.

True it is that under certain conditions, this specific lightness increases the dangers of gas, especially in rooms where it is not laid on, namely, in rooms situated over a spot traversed by gas pipes. Under these circumstances even the street mains may become a source of danger in the event of a breakage during frosty weather. In such case the gas, unable to escape through the frozen crust, makes its way into the lower rooms of the adjacent dwelling-houses, the internal warmth of which produces an indraught of air from the soil. In this manner gas may easily make its way into a house where there are no gas pipes, especially along the water pipes or drains, or through structural defects. At the same time the possibility of an explosion is facilitated by the fact that, in its passage through the soil, the gas loses a good deal of its characteristic smell, and therefore is less easily detected than usual.

In premises where gas is left burning all night in draughty places, the flame must be protected so as to preclude the risk of accidental extinction by the wind; otherwise an escape of gas, extending over many hours, may lead to an explosion.

Frozen gas pipes should be thawed out by means of hot water or other heated articles, and never by naked lights.

In all establishments where dangerous liquids, gases, or dust are treated, and gas is used for lighting (even though not in the rooms where such treatment is performed), a Muchall testing apparatus should be installed, at the front end of the line of gas pipes, in order that any leakage may be detected at once. Should a smell of gas be noticed, the site of the escape should be sought for by means of a solution of soap, never with a naked light.

The explosive power of mixtures of coal gas and air is destroyed by the presence of 7-10 per cent of carbon dioxide.

### 3. Oil Gas

Oil gas, or fat gas, behaves in general like coal gas, except that the flame is more readily blown out by the wind, a circumstance that may lead to the danger discussed above. Hence the burners used for oil gas should be properly shielded from draughts.

Oil gas will not stand passing through long lengths of pipe, and is therefore only suitable for small establishments. The troublesome purification, necessary in the case of coal gas, is dispensed with in making oil gas, and consequently the process is simpler and safer, though the occurrence of explosions, due to the sudden disengagement of the gas, is by no means impossible.

On the other hand, oil gas plant is more dangerous than that for coal gas, in respect of the storage, the raw material, and the waste fat or oil (see also under *Lighting*).

## CHAPTER XXI

### ACETYLENE GAS. (See also *Carbide*)

Density 0.92-0.96, *i.e.* almost the same as air.

WHEN calcium carbide is thrown into, or even moistened with, water, acetylene gas is immediately formed. This gas ignites at 480° C., explodes at 509°-515° C. and burns with a flame temperature of 2260° C. It has a strong smell and liquefies at zero under a pressure of 21 atmos., or at 20° C. and 42.8 atmos. pressure.

Acetylene, which, according to Pictet, "is destined to light the whole world," is about the most inflammable gas known, and is also the most explosive, when liquefied or mixed with air, oxygen, or nitric oxide. Liquid acetylene forms a dangerous blasting material.

The chief danger of this gas consists in the fact that its mixtures with air, in almost any proportion, are explosive. The limits of explosibility are wider than with any other gas; thus:—

In Mixtures of Air with	Explosion Commences	And Ceases
Acetylene . . .	with 3 per cent.	with 82 per cent.
Ethylene . . .	" 4 "	" 22 "
Methane . . .	" 5 "	" 16 "
Hydrogen . . .	" 7 "	" 75 "
Coal gas . . .	" 8 "	" 23 "
Water gas . . .	" 9 "	" 55 "
Carbon monoxide . . .	" 13 "	" 75 "

Hence a greater number of explosive mixtures can be formed with acetylene than with any other gas. The zone of maximum explosibility lies between 7 and 11 per cent. of acetylene.

Another danger of this gas consists in its tendency to decompose into its elements, hydrogen and carbon, the heat evolved during the process being as great as that developed by the combustion of an equal volume of hydrogen, the hottest burning gas known. This heat is absorbed by the liberated hydrogen (the carbon being condensed to the solid form), with the result that the gas expands to such an extent as to cause a powerful explosion.

Though acetylene can be ignited and decomposed by electric sparks or incandescent bodies, mercury fulminate, or flame, the decomposition is confined to the immediate vicinity of the igniting factor when the gas is contained in closed vessels, and does not spread to the entire volume of gas, *i.e.* pure acetylene in closed vessels is inexplosive. This property, however, vanishes as soon as the pressure exceeds that of the atmosphere. In all other cases, especially above 2 atmospheres pressure, the decomposition is transmitted throughout the entire volume of the gas in less than  $\frac{1}{1000}$  of a second, *i.e.* acetylene stored under pressure is explosive, and in this condition acquires an explosive force equal to that of the most powerful blasting materials.

The final pressure produced by the explosion depends on the initial gas pressure. If the latter be  $2\frac{1}{2}$  atmos., the former will attain 10 atmos.; with 6 atmos. it rises to 42 atmos.; and with 21 atmos. to 210 atmos. Hence the greater the storage pressure the higher the explosion risk.

If the pressure be increased to such a degree as to liquefy the gas, the smallest initial decomposition (from the aforesaid causes) spreads with the utmost rapidity, and explosions of the most violent character imaginable (often with a pressure of 5000–6000 atmos.) result.

Attempts have been made in practice to tame this highly explosive liquid, its chemico-technical value being too great for its dangers to frighten off endeavours to utilise it for industrial purposes; but none of the experiments in this direction have proved fully successful. Much, it is true, has been accomplished, but not all; and fresh vagaries are continually being manifested by Pictet's universal illuminant, which really seems more likely to blow up the whole world than to light it.

Acetylene explosions are not merely extremely violent (most of them resulting in loss of life), but also often of a very puzzling character; and before the gas can come into general use as a trustworthy industrial agent, many experiments will have to be made and its nature more fully investigated.

Between the years 1897 and 1900, the number of explosions amounted to 32, 17, 5·4 and 2·2 respectively per thousand users of the gas. Though a considerable improvement must be admitted, the most favourable figure, 2·2 per mil. still indicates a high risk.

It must be granted that many of the accidents have been due to carelessness and ignorance, and for these the gas should not be blamed. Nevertheless, these two factors were precluded in many cases of highly puzzling character and extreme gravity. It has even happened to Pictet, the best connoisseur and most zealous investigator of acetylene, to have his plant destroyed twice over—on 17th October and 4th May, 1896—by acetylene explosions and the resulting fires.

Not only is acetylene rendered dangerous by pressure, but also by other factors, though not to the same extent.

**Concussion, Fall.**—Pure gaseous acetylene in strong vessels (but not subjected to a pressure of more than 10 atmos.) may be exposed to powerful shocks, blows, falls from a considerable height, and the effects of gunshot, without exploding, provided that no sparks are produced and no gas can escape from the vessel. On the other hand, the presence of liquid acetylene in the vessel will cause a violent explosion under the above treatment.

**Heat.**—When heat is applied, whether locally or broadcast, to pure acetylene in a closed vessel, the effects are the same as those of direct ignition, electric sparks, &c., and explosion may result even if the gas be under merely moderate pressure. All vessels containing acetylene should be protected from the action of heat, since the gas should *never* be heated above 35° C. (see *Acetylene Apparatus*). The ease with which acetylene can be ignited by heat may be demonstrated by a simple experiment. If an acetylene burner that has become hot through the burning of the gas be extinguished, and the tap immediately turned on again, the outrushing gas will light of itself by contact with the hot burner.

**Sparks.**—Anything likely to produce sparks (friction, shock, bursting of apparatus, &c.) is a source of danger to acetylene kept under pressure.

Through the sudden opening of the delivery apertures of vessels containing acetylene under pressure, the escaping gas may become so hot as to take fire. The overcharging of the vessels that are not sufficiently cooled, or the transfer of acetylene from a small vessel (under pressure) to a larger one, is also a source of danger.

The presence of spontaneously inflammable phosphuretted hydrogen gas, or the formation of an incrustation (consisting of a little-known greyish black substance, with a tendency to spontaneous ignition) within the vessel, will contribute appreciably to the increase of the explosion risk.

This incrustation, consisting of a hydrocarbon, will ignite spontaneously when merely compressed or slightly warmed; *i.e.* it assumes the gaseous form, and should this occur in a closed vessel, the bursting of the latter may ensue.

Attempts to render liquefied acetylene innocuous have been abandoned; in some countries (England among them) the use of acetylene in this form is prohibited. Attention is now confined to the safe employment of gaseous acetylene under moderate pressure.

The tendency of acetylene to ignite spontaneously when it contains phosphuretted hydrogen, may be obviated by using carbide free from that impurity. Danger is caused by as little as 0.02 per cent., but larger proportions have been detected in the carbide. In such cases a slight vaporous cloud is formed in the air of the room where the acetylene is burning: an indication of this impurity, which should be removed by a thorough purification of the gas.

To guard against explosions, &c., arising from leakages in the storage vessels, pipes, &c., these latter must be constructed with extreme care and of best materials only.

Owing to the relatively high pressure in the pipes entailed by the necessary employment of very minute burner orifices, the danger of acetylene leaking through defective joints is increased, the loss from

this cause being about 15 per cent. as compared with 7 per cent. in the case of coal gas.

The use of rubber piping or rubber bags for the conveyance or storage of acetylene should be prohibited, since the gas is able to penetrate airtight rubber; so much so indeed that it has been found by experiment that the smell of the gas becomes apparent in half-an-hour, and the whole of the acetylene escapes in about five days.

To prevent acetylene lighting back from the burner jet to the generator, at least two non-return valves (*e.g.* Berdenich valves) should be provided, one between the generator and the gasometer, and one between the latter and the pipe leading to the burner. Almost equally effective is the use of small vessels, filled with asbestos between wire gauze and placed in the positions mentioned.

It is sometimes important to determine the presence of small quantities of escaping acetylene in the air of closed rooms. This may be done by means of the hydrogen test, which will also serve to locate leakages in the pipes, a point of special importance in rooms where the smell of the acetylene is masked by other odours, or where dangerous substances or gases are produced or employed.

To apply the test the lights are turned down, and a small hydrogen generator is operated. After all the air has been expelled from the generator the escaping hydrogen is ignited, and the flame is adjusted to a length of ten millimetres exactly. The presence of acetylene causes an elongation of the flame, 0.25 per cent. increasing the length to 17 mm., 0.5 per cent. to 19 mm., 1 per cent. to 28 mm., and 2 per cent. to 48 mm.

Successful attempts have been made to diminish the dangers of acetylene by admixtures of other gas. Thus the most highly explosive mixture of 11 per cent. of acetylene and 89 per cent. of air is rendered inexplosive by the addition of 20 per cent. of carbon dioxide or nitrogen; but, since these two gases diminish the illuminating power of the acetylene, they have been replaced by other illuminating gases, the best for the purpose being coal gas and oil gas. The latter in particular is now used in admixture with acetylene, in the proportions of 1 : 1 or 2 : 1, *i.e.* 50 per cent. of acetylene and 50 per cent. of oil gas, or 60–65 per cent. of oil gas and 40–35 per cent. of acetylene. In addition to being inexplosive, these mixtures may be subjected to a pressure of 6 atmos. without attaining the explosibility of pure acetylene. Whether the danger increases at higher pressures has not yet been ascertained; at any rate considerable caution is advisable when 6 atmos. is reached. Acetylene is not well suited for incandescent lighting, the mantles being rapidly injured and spoiled by the violence of the detonations on lighting the gas.

For technical purposes the dangers of acetylene have been reduced by dissolving the gas in liquids that are capable of absorbing it in large quantities. Water is unsuitable for this purpose, since it merely dissolves its own volume of the gas; and, besides, this solution is always dangerous when brought into contact with burning gases or oxygen. Hence all water containing acetylene, and especially waste waters that have stood in contact with the gas for some time, must be handled with care. Such water is met with in every acetylene plant, *e.g.* the water from the gas scrubbers, from the gasometers, generator, meter, and that

from the water seals. These must all be discharged in some place where they cannot do harm, but can either drain away quickly or be diluted with sufficient running water to make the contained acetylene of no account, since cases have been known where even small residual traces of acetylene have produced violent explosions, and that too after a considerable interval.

The dangers of acetylene waters can best be obviated by replacing the water by brine for the purpose of scrubbing the gas, forming the water seals, charging the gasometers, the vessels and the meters, since acetylene is insoluble in a brine containing 15–20 per cent. of common salt.

Neither is alcohol suitable for the purpose of dissolving acetylene, though it will take up six times its own volume of the gas. This quantity, however, is insufficient for technical purposes, and, moreover, the alcohol itself is a source of danger, owing to its inflammability and the ease with which it liberates explosive vapour when warmed.

The best solvent is acetone (*q.v.*). Under ordinary pressure, this liquid will take up 31 times its own volume of the gas; and if cold be employed, one part of acetone will absorb, at  $-81^{\circ}\text{C}$ . (the solidification point of acetylene), as much as 2000 parts of acetylene, its own volume being thereby increased 4–5 fold. Even under pressure alone—though this is dangerous—the solvent capacity can be raised to 50 volumes of acetylene to one of acetone.

These industrially applicable solutions of acetylene in acetone are far less dangerous under pressure than pure acetylene; for, whilst the latter is highly explosive at a pressure of merely 2 atmos., the solution may be exposed to a pressure of 10 atmos. without any great danger being incurred. Endeavours have also been made to minimise the risk of explosion by absorbing the solution with kieselguhr, as in the case of nitroglycerin. Further experience in this direction is still lacking.

One point, however, must be noted, viz.:—If the acetone be super-saturated with acetylene, so that free gas accumulates in the container, this gas will present the same dangers as acetylene gas generally. Care is therefore necessary not to charge the acetone with any more gas than it can properly dissolve.

The containing vessels for such solutions must fulfil the same conditions as those used for storing liquefied gases, and must be strong enough to resist the highest pressures, because a very moderate rise in temperature will increase the pressure.

Since pressure is employed, as well as cold, in dissolving acetylene in acetone, the pressure in the storage vessels always amounts to about 6 atmos. Assuming this pressure to obtain when the temperature of the vessel is  $14^{\circ}\text{C}$ ., it will increase

at  $35^{\circ}\text{C}$ . to  $10\frac{1}{2}$  atmos.

$50^{\circ}\text{C}$ . „ 14 „

$75^{\circ}\text{C}$ . „  $20\frac{1}{2}$  „

Hence these storage vessels must be protected from heat, especially the sun's rays, and temperatures above  $30^{\circ}\text{C}$ . which are of not infrequent occurrence during the summer. The greater care is necessary, inasmuch as acetone itself (*q.v.*) is a somewhat dangerous substance.

The experiments conducted by G. Claude and others, on the explosibility of solutions of acetylene in acetone, have shown that the immersion of glowing metal in the solutions does not produce an explosion; though other experimenters again have obtained violent explosions under identical conditions. Great caution is therefore desirable under all circumstances, and the dangers resulting from the contact of glowing metals with the solutions in question should not be too lightly esteemed.

All these remarks must be understood to refer to acetylene that is at least technically pure. Since, however, the carbide used for generating the gas is generally very impure, the product is usually contaminated, chiefly by such gases as sulphuretted hydrogen, ammonia, phosphuretted hydrogen, hydrogen silicide, carbon monoxide (all derived from the lime and carbon). Nitrogen and oxygen are also present, being derived from the air occluded in the porous carbide.

Mention must also be made of benzol vapours and tarry products, which form when the acetylene becomes strongly heated as a result of being disengaged at a too rapid rate, or when the apparatus is charged with carbide beyond its normal capacity.

Owing to the highly divergent nature of these gaseous impurities they cannot be eliminated by simply scrubbing the acetylene with water, and even the necessary chemical purification involved does not always suffice. Washing, however, must on no account be omitted, and every acetylene plant must be fitted with a scrubber for that purpose. The chemical purification consists in passing the gas through solutions of acid iron and copper salts, cupric chloride being particularly efficacious in the removal of phosphuretted hydrogen. Chromic acid has a good effect, and other useful purifiers comprise: mercury salts, chloride of lime and lime salts, and sodium bichromate, the latter somewhat acidified and used in conjunction with diatomaceous earth (kieselguhr).

A very pure gas is said to result from the use of sodium silicate solution, instead of water, for generating the acetylene. This reagent is also said to keep the temperature of the liberated gas (which may otherwise attain 100° C.) down to 38° C., and thereby furnish a product of high general purity. There are also a number of secret commercial preparations for purifying acetylene, one of which, puratylene, is said to be highly efficacious. The percentage of sulphuretted hydrogen in the gas decreases concurrently with the amount of heat disengaged by the carbide in the production of acetylene. The dropping and intermittent immersion systems furnish the most.

It is essential that none of the purifying agents used should liberate chlorine; otherwise the very dangerous product, chloracetylene, is formed, which is exploded by direct sunlight.

The purifiers should be used in the form of solutions wherever possible; otherwise as powder, employed in such a manner as to preclude balling under the influence of moisture, since this may readily lead to obstruction in the apparatus, the resulting pressure being always a source of danger. A still more dangerous form of obstruction arises from the freezing of the water in the generator, gasometer, purifier or meter, during the winter. This may be prevented by heating the room with steam or hot air (never by open fires), or by dissolving various salts in the water used. Such salts include common salt and magnesium chloride, also glycerin; but they must be pure, or the apparatus will suffer corrosion.

A new material for this purpose is known as antiglacid. This does not freeze above  $-60^{\circ}\text{C.}$ , or, when mixed with water

in the proportion 1 : 2, at  $-5^{\circ}\text{C.}$ ,  
" 1 : 1, "  $-16^{\circ}\text{C.}$ ,  
" 2 : 1, "  $-23^{\circ}\text{C.}$

The second mixture (1 : 1) is sufficient for the purpose, provided the acetylene apparatus is not exposed to very severe cold.

All premises where acetylene is used for the preparation of acetylene compounds in addition to lighting are dangerous establishments, both the new compounds and the chemical reactions involved being dangerous. It must therefore be ascertained in every case where acetylene is in question whether the same is used exclusively for lighting or for other, chiefly chemical, purposes.

Special danger attaches to the compounds of acetylene with silver, copper, and mercury. These, however, are not produced by direct contact between the gas and the metals, but only when the latter are already corroded by rust, and when the combined action of moisture and ammonia is in question. Ammonia is almost invariably present in acetylene, and contributes to the formation of these dangerous products.

The objections to copper and brass fittings for acetylene apparatus are unfounded, provided they are kept in good condition, clean and bright; only, the vessels must not be entirely constructed of these metals. The acetylene compounds of mercury, silver, and copper are explosive only when dry, but the explosion is then extremely violent, and occurs under the influence of shock or heating to about  $120^{\circ}\text{C.}$

Recently a distinction has been drawn between the acetylene-copper compounds prepared by the wet and dry methods respectively. Copper acetylide prepared in the dry way can be heated to  $60^{\circ}\text{C.}$  in acetylene gas without exploding; whereas that obtained by the wet method explodes spontaneously in acetylene gas, hydrochloric acid gas, or sulphuretted hydrogen, though not in carbon-dioxide or hydrogen. This phenomenon has a certain scientific interest; but in practice it is less easy to control the method of formation, and therefore the metallic compounds should invariably be regarded with suspicion.

Special attention is merited by the mixtures of chlorine gas with acetylene. When acetylene is introduced into gaseous chlorine, the latter burns at once and without explosion; but on reversing the procedure and introducing the chlorine into the acetylene, a most violent explosion ensues almost immediately. Both phenomena are spontaneous and are furthered by direct sunlight.

Of establishments employing acetylene for other than lighting purposes, special mention should be made of lampblack factories, wherein finer grades of black are produced by the sparking ignition of acetylene. As the gas used for this purpose is under a pressure of 2-3 atmos., its ignition by electrical means is attended with considerable danger.

Many explosions have occurred through the faulty construction and careless handling of the apparatus, proper construction and careful management being essential conditions in the manufacture of acetylene. It is too often the custom to look upon the apparatus as a secondary matter altogether, and to set it up in a stable or wood shed, the working

being left to the care of some one entirely ignorant of the nature of this dangerous gas.

The reason for this is to be sought in the simplicity of the method of preparing acetylene, which seems to be child's play in comparison with the production of coal gas or electricity. Though the mere addition of water to carbide effects the disengagement of the gas, the method of bringing the two into contact, simple as it may appear, has a considerable influence on the dangerous character of the resulting gas.

At the present time there are three chief systems in use:—

1. Water is allowed to fall on the carbide, drop by drop (the dropping system).

2. The water is allowed to rise to the carbide (dipping or suffusion system) and then subside again (automatically).

3. A quantity of carbide is thrown into a larger quantity of water (immersion system).

In the first case the considerable amount of heat disengaged in the formation of the acetylene is imparted to the fragments of carbide, in the absence of any other substance. The extent to which this heating of the carbide may proceed in the dropping system is shown by the following results of experiments, made by gradually dropping 350 cc. of water on to 227 grms. of carbide. The dropping occupied 60 minutes, and the carbide attained—

in minutes:	1	2	3	7	10	13	20	27	37	47	60
a tempera- } ture of: }	97°	154°	209°	244°	317°	644°	600°	497°	420°	373°	C.

Thus, in twenty minutes the fragments of carbide attained red-heat, and since acetylene ignites at 480° and explodes at 509°–515°, accident from these causes is not precluded when the acetylene surrounds fragments of carbide at such high temperatures.

The danger of spontaneous ignition in this dropping system is considerably diminished when the charge of carbide in the apparatus is small. Generally, however, the apparatus is filled as full as possible to save trouble; and that is just the way for the maximum temperatures to be developed. The heat is greatly reduced when water is replaced by a solution of sodium silicate; and this applies also to the dipping system.

Dropping systems are always dangerous.

In the second case the danger of spontaneous heating is still greater than in the first, temperatures as high as 800° C. having been observed in the carbide. This increase of heat is due to the circumstance that, instead of only a small part of the carbide being in contact with the water at any one time, as in the dropping system, here the whole of the carbide is diffused with water, and is then removed from contact as soon as the liberation of acetylene is desired to cease. The whole of the carbide being moistened at once, the evolution of gas is very rapid; and when the carbide is out of contact with the water, the whole of the heat acts on the former and may raise it to incandescence. In this event the danger of the acetylene becoming ignited is the same as in the dropping system, only more so.

In addition there is the risk of protracted liberation of the gas, inasmuch as the water that has entered into combination with the lime

during the decomposition of the carbide may be attracted by the still undecomposed portions of the carbide and produce a further disengagement of the gas.

The occurrence of this phenomenon indicates that the carbide has attained a temperature of at least  $420^{\circ}\text{C.}$ , since it is not until this point is reached that lime will part with its water.

This after-liberation of gas is a source of danger when the apparatus is no longer working, since pressure then ensues within the closed apparatus, and any accumulation of acetylene under pressure is always more liable to explode. The only effectual method of counteracting this risk is to provide a safety valve leading into a long pipe that discharges above the roof.

In the immersion system, where a relatively small amount of carbide is immersed in a large volume of water, the risk of spontaneous heating is entirely precluded, the water taking up the whole of the heat evolved. When the proportion is 5 parts or less of carbide to 100 parts of water, not only is the spontaneous heating of the carbide or the ignition of the gas impossible, but all possibility of the after-liberation of the gas (see under 2) is entirely removed. This system, though not automatic like the other two, is the safest of all.

The so-called automatic apparatus have always some objectionable features; they frequently get out of order, and every failure to act is a source of heightened danger and increased possibility of explosion. Hence none but the simplest form of apparatus should be chosen, that does not require skilled attention or complicated repairs and is little likely to get out of order.

Official regulations have already been drawn up for obviating the dangers of carbide and acetylene plant. To these regulations the reader is now referred, and all that will be gone into in this place are the principal precautions with respect to such plant and the places where it is set up.

The entire installation must be constructed and erected in the most careful manner. Purifiers and scrubbers for the gas must be provided. Safety valves, for the prevention of internal pressure, are essential. There must be two non-return valves: one between the generator and the gasometer, the other between the latter and the delivery pipes. Some device must be provided for the secure removal of the spent lime, which still contains particles of carbide capable of liberating gas. The waste materials and water containing acetylene must be removed. The calcium, and other carbides and carbide waste, must be kept dry and stored in a fireproof manner. The attendants must be thoroughly instructed on the nature of carbide and acetylene. Only closed lights, or safe external lighting should be allowed. The rooms containing the apparatus must be thoroughly ventilated, both at roof and floor level. The only heating arrangements permissible are with steam, warm water, or hot air; never with open fires. Where no system of heating is possible, the apparatus must be protected from frost. Pure carbide should alone be used. Notice must be posted at the entrance, prohibiting admission to unauthorised persons, smoking, and the use of naked lights. The room containing the apparatus must be kept under lock and key. Preference should be given to apparatus of the immersion type.

The question whether acetylene explosions are capable of starting

fires may be generally answered in the negative. These explosions are extremely violent, but do not produce much flame nor are they highly igniting in character, unless any particularly inflammable substances are present in the same room (which must be prohibited). The presence of explosive substances, however, is the more objectionable, inasmuch as the great violence of the acetylene explosion may be transmitted to these substances and cause them also to explode.

In connection with acetylene explosions, the following instances may be mentioned: in one case an escape of acetylene occurred in the room where the plant was installed. The owner of the premises, desiring to remedy the inconvenience by opening the door, struck a match in order to be able to find the keyhole more easily. A violent explosion instantly ensued, the gas having escaped through the keyhole. A similar explosion was occasioned by the gas escaping through a leak in the window and coming into contact with a light outside.

These instances indicate the necessity for great care in the use of uncovered light or flame, even in the vicinity of rooms where acetylene is being generated.

## PART IV—DANGERS IN VARIOUS ESTABLISHMENTS

### CHAPTER XXII

#### PHARMACEUTICAL CHEMISTS' AND DRUG STORES

THE risk of fires and explosions in these establishments has been considerably diminished since the custom has arisen of purchasing most of the preparations ready-made, instead of preparing them on the premises as formerly. On the other hand, the risk incurred by the storage of explosive medicinal preparations, cosmetics, and bandages, has even increased.

The presence of really dangerous and even explosive ingredients in these preparations has been practically demonstrated in not a few instances. For instance, the mixtures of potassium chlorate with catechu, gall nuts, or tannin; of chromic acid and glycerin; iodine and ammonia, are all somewhat explosive in character. Chlorate pastilles (containing potassium chlorate) kept loose in the pocket may explode by friction against knives, keys, or other hard articles. Chlorate also explodes much more violently when loosely mixed with sugar or similar organic substances.

Hoffmann's drops consist of a highly inflammable liquid of low boiling point, and disengaging ethereal vapours.

Most anæsthetics boil at very low temperatures, not far removed from that of the body. They are prepared from: petroleum ether (b.p. 40°–70° C.), ether (b.p. 35½° C.), and chloroform (b.p. 61° C.), the average boiling point of the mixtures being 38°–42°. Other ingredients include ethyl bromide (b.p. 39° C.), methylene chloride (b.p. 42° C.), pental (amylene) (b.p. 38° C.), methylal (b.p. 42° C.), æther anæstheticus Koenig (b.p. 26° C.), nitrous ethyl ether (b.p. 16·5° C.) All of them produce great cold in evaporating.

The greater the volatility and cold-producing property of these substances the more extensive their employment as soporifics and anæsthetics. For this reason even the low-boiling (11° C.), dangerous ethyl chloride (Henning) is often used as an anæsthetic, though with the precaution of fitting the tube with a clamp so arranged as to permit the escape of only just enough vapour to produce anæsthesia. It is very dangerous to allow this substance to vaporise freely.

The same precaution must be adopted with the mixture of ethyl- and methylchlorides known as Anestile Bengué, which boils even at zero C.

Danger is incurred wherever such preparations are made, stored, packed, or used; and in the event of fire, stores of these materials may cause extremely violent explosions.

The application of these and similar anæsthetical preparations must be restricted to well-ventilated rooms (sick rooms, operating theatres, clinics) from which all naked flames are excluded.

Great danger attends the mixing of iodovasogene with alkaline, ammoniacal substances, on account of the possibility of nitrogen iodide (*q.v.*) being formed.

The much-advertised washes for the head and mouth are mostly alcoholic or ethereal solutions of antiseptic substances, such as oils, ethereal oils, salts, acids, salol, &c. As only a few drops at a time are sufficient for use, these preparations contain a good deal of ether and alcohol; and as they consequently flash at 14°–20° C., they are usually highly inflammable, whereas those compounded solely of glycerin and soap solution are perfectly harmless.

Shops with open lights and with large stocks of such dangerous cosmetic preparations may easily suffer from extremely violent explosions in the event of fire.

Bandages are frequently impregnated with solutions of celluloid (*q.v.*), in acetone, and are therefore very highly inflammable, flaring up violently, though they rarely explode.

Liquid detergents, or grease eradicators, chiefly consist of benzol, though ether is occasionally present. When stocked in large quantities they constitute a source of danger to shops, show windows, and drug stores.

There are various innocuous grease eradicators, such as carbon tetrachloride, ammonia benzine soaps, chloroform, ox gall, pipeclay, fat balls (these last two act by absorption rather than solution), but their efficacy is far inferior to that of benzol and ether. The preference accorded the two latter is due to the greater ease with which every spot of grease is removed by their solvent action than is possible with absorbents.

One of these preparations, known as benzolinar, consists of coal tar benzol with about 20 per cent. of ether and traces of ethereal substances. (In general the composition of these preparations often varies.)

Premises where these substances are prepared, stored, or used are exposed to still greater risks of fire and explosion; such an accident may follow the breaking of a bottle in a show window illuminated with open lights.

The so-called "Benzol-polysolves," consisting of benzol and dissolved soap in suitable proportions, are less dangerous; and solid benzol soaps are perfectly safe.

Other dangerous substances kept or used by apothecaries and drug stores are discussed under their proper headings.

## CHAPTER XXIII

## LABORATORIES

A DISTINCTION, as regards the risk of fire and explosion, must be drawn between commercial, pharmaceutical, works, explosives, and university laboratories.

Laboratories where explosives are dealt with may be omitted from consideration here, since they will hardly form objects of insurance, whilst in other laboratories the testing of explosives on any large scale is, or should be, prohibited.

### 1. Commercial Laboratories

differ from all other kinds (except university laboratories) inasmuch as, apart from explosives, all sorts of tests are performed, whereas in other laboratories the work is confined to testing the products, &c., of the particular factory. The only exception to this rule is afforded by university laboratories, which generally have a large number of workers who are mostly deficient in knowledge and therefore likely to endanger the establishment by some error. The author recalls an instance in his own experience where a young student secretly prepared about 10 lbs. of nitroglycerin, and would certainly have caused immense damage owing to his defective acquaintance with the nature of this substance.

### 2. University Laboratories

more nearly resemble small factories, or experimental works, a fact necessitating the provision of effective control by assistants.

All laboratories should be of fireproof construction, especially as regards the roof, walls, and floor, so that no danger from fire may result from the performance of experimental work attended with any degree of risk. With this object the walls and roof should be coated with at least an inch of lime plaster, and no exposed woodwork should be allowed.

Special rooms of fireproof construction should be provided for all operations involving the use of sulphuretted hydrogen, oxyhydrogen gas, the performance of ultimate analysis or combustion tests, experiments with bombs and fused glass tubes at high temperatures and pressures, crucible work, calcination, and nitration. Where coal gas is not available, ultimate analysis and combustions may be performed with small benzine, ligroin, or gasoline apparatus, the vapour from the combustible liquid being delivered to the combustion furnaces by the pressure generated by a pump. In working these apparatus certain precautions are necessary: they must be fitted with a pressure gauge, and the pressure must not exceed about 7 lbs. per sq. inch; the use of benzol should be prohibited; and the apparatus should be set up at a safe distance from the furnaces, on account of the great heat radiated from the latter, a protecting partition of boards or sheet-iron being erected between them. The evaporation of inflammable solvents (ether, benzol,

carbon disulphide, &c.) must be effected in suitable draught closets or in the open air, and solely by means of a water bath or other heating liquid.

### 3. Heating Baths

comprising water baths, saline baths, sandbaths, asbestos baths, oil baths, paraffin baths, and baths of molten metal, must be handled with a due amount of care, and, as they are often left for hours without supervision, should be set up in fireproof places only.

The following are the maximum temperatures to which these various baths may be heated :—

100° C., water.	
104°–105° C., soda solution	} Saline baths.
115°–116° C., saltpetre solution	
124°–125° C., sodium acetate	
135° C., potash solution	
180° C., calcium chloride	
300° C., sulphuric acid.	
335° C., metallic lead.	
370° C., paraffin oil.	
400°–600° C., air, sand, ashes, asbestos.	
373° C., anthraquinone.	
448° C., sulphur.	
518° C., phosphorus sulphide.	
606° C., stannous chloride.	
650° C., zinc bromide.	
730° C., zinc chloride.	

The safest of these baths are those charged with water, salts, sand, asbestos, or ashes, the metallic baths (lead and tin) being more dangerous on account of the relatively high temperatures to which they may attain (lead up to 1600° C.); whilst the most dangerous of all, in respect of inflammability and the liberation of combustible vapours, are the oil and paraffin baths.

Other sources of danger, for the most part less important, in laboratories, can be obviated by the following precautions :—

Explosive and inflammable reagents, chiefly liquids, should only be kept in the laboratory in small quantities sufficient for daily use (about  $\frac{1}{2}$  litre). The reserve stock should be kept cool, in fireproof store-rooms, and if necessary separate from one another.

The furnaces must be far enough away from the work-benches, and ample ventilation must be provided.

The lights must be of such a character as to preclude risk when small quantities of inflammable substances are being used; electric lighting is desirable.

Drying cupboards must be mounted in a fireproof manner. A thorough inspection of the rooms, after work has ceased in the evening, is an essential precaution, especially for university or high-school laboratories.

### 4. Works Laboratories

The fire risk of these laboratories is not always to be judged in accordance with that of the works in question. For instance, very

dangerous work has often to be carried out in the laboratories of establishments that are themselves of a harmless character: dairies, certain colour works, and soapworks; in dairy laboratories large quantities of ether are used, sometimes many litres a day.

Where the operations in any works have a decided fire risk, the laboratory should be isolated from the rest of the premises, to prevent the one endangering the other; since, though there may be little danger arising when the work is properly conducted, a different complexion is put on the case when a laboratory is connected with the works. In the laboratory inflammable substances are being continually handled, even though only in small quantities, and therefore an accident, even though small, may happen at any moment. In the laboratory it is the frequency of danger, in works the extent, that predominates.

A conjunction of these two factors constitutes the maximum of danger, and hence, whenever the laboratory work is of a risky character, this establishment should be isolated from the rest of the premises.

The present is an opportune moment for discussing the general character of the danger arising from the frequent use of small quantities (in the laboratory) and the working up of large amounts of dangerous substances (in the works), and endeavouring to determine which causes the greater risk.

This question is of special importance in the case of liquids like benzol, ether, alcohol, acetone, carbon disulphide, and wood spirit, as also of many substances of explosive character. Importance also attaches to it on account of the prevalent opinion that "the quantity is only small, and therefore there is not much risk." The view, however, that 1 litre of carbon disulphide is less dangerous than 100 litres must be contradicted to a certain extent, in so far as the dangers in question relate to the *chemical character* of the substance.

In working up large quantities of a dangerous substance, pressure is always brought to bear on the management of the works to see that all possible precautions are observed; official regulations, and, of course, those of the insurance companies being stringent in all such instances.

The adoption of precautionary measures diminishes to some extent the frequency of the danger. Other causes operating in the same direction are: uniformity of handling the materials; knowledge of their dangerous character, resulting in increased care on the part of the staff. In a word, it is the amount of material in question rather than its inherent danger that leads to the adoption of stringent precautionary regulations, and hence to the diminution of the frequency of the danger itself.

The gravity of the danger is in no wise decreased by these measures, but remains invariable under all circumstances, though, in the case of laboratories, &c., where only small quantities of these dangerous materials ( $\frac{1}{2}$ –5 litres) are used, there is always the tendency to assume that the danger diminishes correspondingly with the amount.

This prevalent opinion cannot be regarded as unconditionally justified from the chemical standpoint, since here other conditions intervene. In small establishments where the quantity of dangerous material treated is small, less attention is bestowed on the storage of same than when ten times the amount is in question. In the former case the storage packages mostly consist of glass vessels, liable to get broken;

whereas in large works the storage vessels are strong and unbreakable. These small vessels, when in use, are carried or set down close to places where the danger of fire is considerable; they may be upset, knocked about, or heated to a dangerous extent by some adjacent source of heat, and the contents may be filched by unauthorised persons, or mixed with other substances with which they enter into dangerous chemical reactions generating great heat.

These possibilities are reduced or entirely absent in the case of storage vessels in large works, since these vessels are generally few in number and cannot be moved, being too heavy or else fastened down. There is no risk of their getting overturned, and only a very remote chance of breakage.

In large works the transport of the materials from one vessel to another is generally effected by mechanical means, in closed conduits, without shifting the vessels or spilling the materials. When small quantities, however, are in question, the work is usually done by hand, the vessel being raised and tipped, and the materials often wasted.

Again, the influence of a given source of heat on a large bulk of material is insignificant, a correspondingly large amount of heat being necessary to produce a state of danger; on the other hand, the amount of heat necessary to produce the same result with a small quantity of material is itself small.

The greatest caution is also exercised with regard to the lighting and heating arrangements in the case of materials in bulk, closed lights being used when necessary; but with small quantities, little notice, if any, is paid to the methods of lighting or heating, or the presence of open fires.

On the large scale, the use of the workrooms for dealing with other operations is prohibited, whereas with small quantities the manipulation is frequently performed in the same apartment as that of other substances.

A careful examination of these conditions easily shows that the moments of risk are more numerous and frequent where small quantities are in question, and these moments are less counteracted by precautionary measures than is the case with materials in bulk.

Consequently it is not always correct to place a lower estimate on the dangers of working on a small scale simply because the amounts are smaller, *i.e.* to take the mass of the material as the basis of the extent of danger; it is really essential to take also the frequency of the risk into consideration, and this is far greater with small quantities than with large.

If it be permissible to speak of the quantity and quality of danger from fire, one might say of works dealing with large masses of materials that the risks are qualitatively higher, but quantitatively higher in the case of working with small quantities.

When the two, however, are combined, as is the case, for instance, when a laboratory is present *in* the works, or retailing is practised *in* a store where dangerous liquids are kept, then the dimensions and frequency of the danger are united, *i.e.* the maximum condition of danger is established. The safest plan is to isolate every laboratory from the factory proper.

## CHAPTER XXIV

## CHEMICO-TECHNICAL FACTORIES, COLOUR WORKS, &amp;c.

So numerous are the kinds of chemico-technical factories in existence, and so divergent are the materials and products dealt with and prepared, that it would be impossible to consider them all in detail. Each requires to be treated and judged separately, thus differing from all other kinds of works, *e.g.* brick works, breweries, soap works, gas works, manure works, paper works, &c., that have some points in common, namely, the treatment of similar raw materials and the preparation of analogous products. For instance, brick works of all kinds work up clay, loam, and lime; all gas works deal with coal; all breweries employ malt, hops, water, &c. The works themselves may differ, but only in respect of the machinery employed and method of working, not by the materials, intermediate products, and manufactured articles.

This community of raw materials and finished products disappears when we come to deal with chemico-technical works (chemical works properly so-called). For instance, how different are the materials and products in colour works and factories producing alcoholic preparations; in the manufacture of sulphuric acid and that of bleaching powder or vermilion. Factories for the production of blacking, ink, rat poison, or tapeworm vermifuge, are often classed as chemical works (?); but how great are the fundamental differences between these and establishments manufacturing chemically pure reagents.

In order to form an idea of the degree of fire or explosion risk attaching to such establishments it is necessary to investigate:—

1. The danger each of the raw materials is capable of producing during storage or while in use;
2. The same characteristic of the intermediate and final products;
3. The various processes employed: firing, nitrating, oxidising, reducing (with hydrogen), impregnating, burning, briquetting, carburetting, carbonising, kilning, drying, fulminating, gasification, lacquering, refining, distilling, subliming, vulcanising, charring, calcining, incinerating, &c.;
4. The progress of the different operations, whether turbulent, accompanied by the formation of dangerous by-products and waste products, or the liberation of gas, vapour, or dust;
5. The treatment, purification, or storage of waste products or spent raw materials, with a view to their use over again (recovery or revivification);
6. The working temperatures during the various stages of operations (see table).

The degrees of fire risk always differ in chemico-technical works, and can only be accurately defined by a careful analytical examination on the basis of the foregoing six clauses. All establishments of this character must be regarded with suspicion when they decline, for business reasons, to furnish the insurance company with details of the raw

materials used and the intermediate, final, and waste products anticipated, in connection with some new substance or preparation they desire to manufacture or employ.

Under such conditions the progress of chemical reactions on a working scale must not be excluded from inspection, proceed they never so smoothly *in the laboratory*. When working *on the large scale*, quite different and dangerous reactions may arise; hence the risk of insuring such establishments should not be accepted until a summer and winter working season has passed without any accident from fire or explosion.

Great attention should also be bestowed on the workmen's clothing and the places where the same is kept (see *Clothing*).

## CHAPTER XXV

### SUGAR WORKS

THE following operations are attended with risk in these works:—

Sulphuric acid and hydrochloric acid are used for cleaning out the evaporating plant, and these, in conjunction with the residual matters to be eliminated, furnish hydrocarbon gases and hydrogen, the latter as a result of the corrosion of the metal by the acids. Hence a violent explosion of these gases, in admixture with air, may ensue when naked lights are used in inspecting the interior of the apparatus.

On this account it is necessary, before introducing a light, to expel these gases by scalding out the apparatus with boiling water. The most dangerous stage is after the dilute acids have been left for some time to act undisturbed in the apparatus.

The danger of dust explosions is incurred in rooms where sugar is being finely ground and sifted by any means, especially in refineries, unless the grinding and sifting machinery be carefully enclosed, and all chance of the fine dust escaping into the air of the room is precluded, since any naked light will suffice to ignite the floating cloud of sugar dust and induce an explosion.

Explosions may also follow the use of naked lights in shoots or elevators for conveying finely ground sugar; the spilling or shaking of dry, powdered sugar from sacks must be avoided when naked lights are present.

Gases (chiefly carbon dioxide, sometimes accompanied by hydrogen and gaseous hydrocarbons) are liberated at certain times in the diffusion plant, as a result of the fermentation of the sliced beet. The occurrence has also been attributed to the character of the water and to badly grown beet. These gases will ignite and explode in contact with a naked light; and numerous explosions have already occurred from this cause. No danger is produced by the wet spent slices. So-called explosions of the quick-running centrifugal machines are also not uncommon; consequently, these machines should be set up in such a position that an explosion may do the smallest possible amount of damage to the lighting plant. When the dangerous gas is produced by the water, the latter may be purified

by an addition of potassium permanganate, about  $\frac{1}{2}$  lb. of this substance being sufficient for the day's consumption.

In some sugar works the molasses is worked up into concentrated fodder by incorporating it with oily or mealy substances. Experience has shown that these mixtures (see *Agricultural Products*) have a tendency to heat, and even ignite spontaneously. Extensive spontaneous heating, even proceeding as far as internal charring, may occur in dried beet slices, when the same have afterwards become moist and exposed to pressure by piling them in heaps.

The working temperatures in sugar works range from 30° C. (86° F.) to 108° C. (226° F.). In the kilns employed for burning lime and producing carbon dioxide (see *Kiln Explosions*) the usual temperature is 600°–900° C.

## CHAPTER XXVI

### BREWERIES AND MALTINGS

THE dangers attendant on these establishments have considerably diminished since numerous small premises of defective construction have disappeared and given place to those of newer and more perfect character.

The boilers apart, high temperatures are not employed, nor are any high pressures used.

The operations attended with the greatest amount of risk are the following:—

1. The mechanical cleaning of barley and malt furnishes large quantities of dust, which is liable to explode on contact with a naked light. Great stress should therefore be laid on the proper isolation or enclosing of these machines, and on the removal of the dust.

2. Damp barley may become heated, even to the point of internal charring, if stored in large heaps (see *Agricultural Products*).

3. Hops bagged in a damp state may heat spontaneously and char. The drying (104° F.) and sulphuring of hops, by means of burning sulphur, are not dangerous operations, provided they be performed in suitable places and with the necessary precautions.

4. Malt culms, when damp, are very liable to heat and ignite spontaneously on being tightly packed or exposed to pressure.

5. The risk in malt kilns may be considerably augmented by careless management and the absence of any check on the temperature; the highest temperature employed is that of 212° F., in the production of colour malt.

6. The operation of lining beer casks with pitch may lead to highly dangerous explosions (see *Resin and Wood*), and must therefore always be performed in the open air. The risk is greater when the pitch used is prepared on the premises (see *Resin*).

## CHAPTER XXVII

SOAP WORKS, CANDLE WORKS. (See *Working Temperatures*)

IN these works the chief danger attaches less to the process and products than to the raw materials and adjuncts used.

The rendering and purifying of fat and fatty waste is attended with the chance of the material boiling over and catching fire.

The supplementary materials, which are readily inflammable, are also a source of danger: resins, benzol, ether, oil of turpentine, varnish, alcohol, oils, and ethereal oils, used—often in considerable proportions—in the preparation of special soaps.

Somewhat high temperatures are employed in the conversion of fat into fatty acids and glycerin ( $315^{\circ}$  C.), in the distillation of fatty acids (palmitic acid) ( $350^{\circ}$  C.) and in distilling glycerin ( $200^{\circ}$ – $310^{\circ}$  C.). The addition of resin to soap lyes is a particularly dangerous operation, owing to the possibility of very violent reaction (see *Resin*).

The storage of large quantities of more or less fatty substances imparts a by no means small degree of danger to soap and candle works; fires in such establishments, where everything is more or less greasy, are difficult to extinguish, and water must be used with extreme care should large amounts of fatty substances be already in a molten or burning condition.

Small outbreaks of fire are best extinguished by means of fine sand, a sufficient stock of which should be kept in readiness in suitable parts of the works.

Closely connected with soapmaking is the manufacture of candles. For making stearin candles, the fat has first to be melted by steam (at about  $176^{\circ}$  C.), then treated with sulphuric acid, washed, and afterwards distilled at  $294^{\circ}$  C. The resulting hot vapours being highly dangerous, provision must be made for removing such of them as cannot be condensed, by proper fireproof flues.

Special danger arises in making paraffin candles when the raw material, instead of being purchased ready-made, is first recovered from bituminous shale; in this case the risks are higher than with stearin candles. The shale has first to be distilled, the explosive lamp oil eliminated, and the paraffin recovered from the heavy oils by refrigeration and purification with naphtha (explosive). The final traces of the naphtha are then expelled by heat, explosive vapours being formed. Hence the process involves a whole series of dangerous operations, which, however, are avoided when purified paraffin or ceresin is purchased.

## CHAPTER XXVIII

## REFUSE DESTRUCTORS

THE destructors established for destroying domestic (and also trade) refuse in large towns are not yet technically perfect, and therefore do not afford

the degree of safety desired; nevertheless, the progress already made points to the speedy attainment of that desirable result.

The crucial points in connection with these premises, which may by degrees attain extensive dimensions, and which the insurance companies will have to take into consideration, are:—

The accumulation of large quantities of very divergent materials;

The presence of inflammable or smouldering substances;

Mutual incompatibility of the different associated substances, and the consequent liability to spontaneous ignition (oily rags, damp organic matter);

The formation of dust, which may induce explosions.

At present there are three methods of dealing with refuse:—

By burning, which is only economical when the refuse is autocombustible. This property is peculiar to refuse containing a good deal of waste coal (such as is met with in England, the land of wastefulness as regards coal); and in such cases the refuse can be dealt with in destructors, the furnace gases being conducted through long flues in order to utilise their heat for drying and the preliminary combustion of damp refuse. These furnaces will consume from 25 to 35 tons of refuse per week, and are attended with little danger; the temperature fluctuates considerably (from 600° to 1000° C.).

By fusion (Wegener process), with the aid of coal dust fuel, the high temperature generated (up to 2000° C.) effecting a thorough fusion of the refuse. The furnace gases pass away at a temperature of 1200° C., and find technical employment for other purposes. The fused residue may be utilised as slag bricks for various purposes.

By gasification (Loos' process). In this case the refuse is heated only enough to char and gasify it (about 300°–400° C.). The gas is free from carbon monoxide, but will burn when mixed with coal gas.

Hence, by reason of the materials employed, and the high temperatures and inflammable gases produced, all these methods of dealing with refuse are attended with a moderate risk of fire or explosion.

(The dangers of other establishments will be dealt with in connection with the various substances concerned.)

# PART V—DANGERS OF VARIOUS INDUSTRIAL MATERIALS

## CHAPTER XXIX

### PAPER, MILLBOARD, NITRO- AND EXPLOSIVE PAPERS

#### 1. Paper

ALTHOUGH no very high temperatures or specially dangerous substances are employed in paper-making, the process is attended with certain dangers, inasmuch as the raw materials are exposed to many accidents, and the works to some extent constitute risky objects of insurance. Special attention should be bestowed on small paper mills that are for the most part converted water-power corn-mills and are still very primitive in arrangement.

The raw materials, mostly foreign waste (ropes, nets, textiles, rags, paper, millboard, vegetable fibres, animal fibres, &c.) are frequently endangered by the presence of greasy and oily substances (liable to spontaneous ignition), by matches and by dusty substances that give off clouds of explosive dust, or settle down on pipes, boilers, &c., and get charred by the heat of same, or eventually take fire spontaneously. Some of these materials may heat and even ignite spontaneously if piled into high heaps while damp.

All operations in connection with these raw materials must be conducted in isolated rooms, and disinfection is also sometimes necessary.

The further treatment in rag boilers and disintegrators is effected by the aid of steam pressure and rapid rotary motion. The risk of explosion is not altogether precluded, especially in dealing with straw, wood, esparto (in making cellulose, *q.v.*), which are dissociated by boiling in closed vessels under a pressure of 5 atmos. The danger is augmented when adjuncts are employed that may corrode the boilers and vessels (caustic soda). Another method, the sulphite process, is carried on by the aid of sulphurous acid, or calcium sulphite, at 118° C., and in such cases the danger accruing from the burning of pyrites, or sulphur (in making the acid), and the somewhat high temperature (300° C) of the sulphurous vapours, must be borne in mind. In some mills the sulphurous acid is purchased pure in steel cylinders, which must be kept away from all

sources of heat and out of the sun, owing to the high pressure of the contents and the great risk of explosion. Where large quantities of sulphite lye are formed as a waste product, they are often recovered by the aid of quick-lime; this latter substance must be kept strictly isolated in the mill, since, when moistened, it is capable of setting paper on fire (see *Lime*).

Another source of danger is the liberation of inflammable sulphuretted hydrogen gas in the elimination of chlorine (used for bleaching the half-finished paper), by the use of antichlor (sodium thiosulphate); and care must therefore be taken to ensure the safe removal of this gas, or to render it harmless by combustion.

In the elimination of chlorine use is also made of dangerous hydrocarbons, such as benzol, petroleum ether, and coal gas, which substances increase the fire and explosion risk of the mill. Sizing paper with resin solutions is attended with the dangers inherent in these latter. Stringent precautions must also be laid down in respect of the drying-rooms, on account of the danger arising from smoking, the handling of lights, heating apparatus, flues, and sparks from adjacent flues or engines.

At the present time the conversion of paper into numerous useful products occupies a highly important industry. Paper may form a substitute for wood and metals, and for this purpose is converted into a compact form, whereby its liability to ignite and burn is considerably diminished. The author has had an opportunity of inspecting large masses of solidified paper that had been exposed to the full force of a conflagration, and nevertheless exhibited merely a superficial charring, the interior remaining entirely unaffected, whereas adjacent timbers were charred right through.

Attempts have been made to render paper incombustible, especially paper intended for bank notes and documents. These experiments proved a failure; and indeed success can hardly be anticipated, since so long as paper is in sheet form, its organic matter can never withstand great heat. Even if it does not burn it will char, an alteration which spoils it completely. On the other hand, success has been attained in the endeavours to impart such a degree of permanence to written characters and indications of value, or dates on bank-note paper, that the same will remain legible after passing through fire.

A certain power of resisting fire is imparted to paper by the addition of substances like alum, sodium tungstate, asbestos, graphite, or diatomaceous earth; and even where the paper cannot be made directly fire-proof, it may be preserved to some extent by keeping it in wrappers of asbestos or asbestos paper.

Endeavours have also been successfully made to protect paper against the influence of wet and moisture; but the process is not free from danger. The requisite materials are resin, fats, and oils, dissolved in naphtha or other inflammable hydrocarbons. Of the oils, preference is given to linseed oil, which, however, must be well boiled. No less dangerous, in point of fire risk, is the method of impregnation employed.

This consists in dipping the paper into the solution of the aforesaid substances, warmed to 60° or 70° C. and then drying (baking) at 120° C. This disengages the volatile constituents of the substance, and the volatile solvent (benzol, petroleum ether, naphtha, &c.), in the form of

readily inflammable vapour, which forms explosive mixtures with air (see *Varnish*). In this drying process, stringent precautions must be adopted for making the room fireproof, excluding all flame, and providing efficient ventilation, or highly dangerous explosions may ensue.

The danger is less in the case of tracing paper, cold-drawn poppy oil or castor oil being mostly used, and the drying effected in the open, without heat.

Parchment paper, which is prepared from sulphite cellulose, is naturally translucent, as a result of treating it with sulphuric acid, and therefore does not need to be oiled. The only danger, and this is slight, is in the drying of the paper between hot rollers.

On the other hand, the manufacture of waxed wrapping papers entails the use of linseed oil, oil of turpentine, or asphaltum solution, the operation being attended with the same risks as the waterproofing process.

For "photographic papers" and collodion paper, see under *Nitro-Cellulose*.

## 2. Millboard

The manufacturing process is similar to that of ordinary paper, but the raw materials are of poorer quality, and, like the product itself, less inflammable than paper stock.

Tar and tar products are used, in addition to linseed oil, for the same purposes as in papermaking. By direct coating with tar and its products, roofing board and tar board are obtained, the process being a specially dangerous one when, as frequently happens, very hot tar is used, and drying is effected in rooms heated to 158°–176° F. Furthermore, explosions may readily occur, through the liberation of volatile constituents from the hot tar. Efficient ventilation and the exclusion of flame are therefore essential. When a more thorough impregnation is desired, steam is admitted to the drying-room; and this steam escapes laden with volatile tar constituents, which render it very dangerous; hence all flame and sparks must be strictly prevented. Though in some respects this method is more risky than the ordinary process, where the tar simply drips from the suspended millboard, yet the use of steam diminishes the fire risk of the products by removing the volatile and inflammable portions of the tar. A further diminution of the risk is effected when the tar is added to the materials in the making.

In the manufacture of oilboard, the dangerous linseed oil is again employed in a boiled state; and, besides, the dangers of this process, which may be highly objectionable, are increased by forced drying, and occasionally also by the use of varnish.

## 3. Nitro- and Explosive Papers

Of late years paper has been chemically prepared for various purposes. Apart from flash papers (see *Flashing Materials*) there are numerous commercial varieties of paper that exhibit fire risks—from smouldering up to explosion—of a highly objectionable character, on account of their having been nitrated, *i.e.* converted into a substance analogous to gun-cotton, and liable to explode under percussion or during drying. Of these classes of paper the following are specially worthy of mention:—

Perfume papers (Armenian paper, Oriental paper, &c.) are unsized

papers that are nitrated, dried, impregnated with an alcoholic solution of ethereal oils, resins, and essences, and re-dried (explosive vapours). The manufacture of these papers is rendered highly dangerous by the process of nitration, drying, the employment of inflammable substances and evaporation of the solvents in large quantities.

Fumigating papers are not nitrated, but merely dipped in an alcoholic solution of resins or extracts, and hung up to dry. In this case the only source of danger is from the liberated vapours of alcohol.

Firework papers (touch paper) are unsized papers that are dipped in a solution of saltpetre (containing a little lead acetate). Though no inflammable vapours are liberated in drying, the paper itself is highly inflammable and capable of smouldering. The smallest spark will fire this paper, which is even more dangerous than Chili bags (*q.v.*). A similar paper, but slower burning, is prepared by brushing paper over with mixtures of flour, sulphur, charcoal, and powdered zinc or iron, the last two named (*q.v.*) being the source of danger.

Detonating papers are nitrated and then coated with potassium chlorate, picric acid, picrates, and charcoal. The preparation is very risky, and the paper highly explosive.

Bengal light papers are not very dangerous, being chiefly prepared by impregnation with harmless chemicals, which, in burning, impart their characteristic coloration to the flame, as in the case of coloured fireworks. In order to increase the inflammability, and produce a flash-like combustion, the paper is often treated with an alcoholic solution of potassium chlorate. When large amounts of this substance are used, the process and product may acquire highly dangerous properties.

Pyrographic papers: a design is drawn with a solution of ammonium chromate, saltpetre, or similar substances, on paper, and remains invisible. When a glowing match is applied to the dried paper, the parts treated with solution immediately begin to glow, and the pattern, &c., is gradually revealed. Such papers are, in themselves, comparatively safe, if well protected from flame or sparks.

The chief danger consists in the circumstance that, should a packet or stock of such paper be accidentally ignited, it may continue to smoulder internally for a long time, without any external indication of its condition. It is only—and then often too late—when the smouldering paper has become heated to igniting point, that the fire is detected (see *Flashing Materials*).

## CHAPTER XXX

### WOOD, WOOD CELLULOSE (Organic Matter)

#### 1. Wood

Wood is the chief representative of organic substances, and what is stated here with reference to its combustibility and behaviour in presence of flame and red heat, applies to the allied organic substances generally. The latter, though differing considerably from wood in their

physical characteristics, resemble it in respect of the chemical reactions produced by heat, flame, &c. These reactions are expressed as desiccation, browning, charring, and incineration, and up to the last-named stage are accompanied by the liberation of gases and vapours, and the formation of liquid products and carbon.

The term organic matter comprises all agricultural concentrated fodders, manures, fertilisers (except those of a purely mineral character, like Thomas slag, kainit, &c.), all vegetable products, fruit, seeds, wood, woody substances (cork, cellulose), all kinds of flour and starch, all animal substances, such as meat, blood, hair, hides, leather, parts of the body, horn, urine, excrement, fat, glue, albumin, bones, and teeth (in part); and all textile materials, fibres, rags, &c. (Wood has already been referred to under *Fireproofing*.)

## 2. Behaviour of Wood in Fire

There is a general tendency, both in daily life and also in insurance, fire-brigade, and judicial circles, to regard the term wood as implying combustibility and danger from fire. Technically speaking, this is correct, since all wood and everything woody and organic is combustible, sometimes readily so, and liable to destruction by fire, whereas stone and metal are typical of incombustibility and indestructibility.

If, however, we subject these three substances—wood (of organic nature), metal, and stone (inorganic matter)—to close comparison, by examining their respective behaviour in presence of fire and heat, we shall find that, in many cases, the organic substance, wood, exhibits the greater power of resistance.

In combating fire, *i.e.* flame and incandescence, it is not only necessary to effect its extinction or prevent transmission to other objects, but also to combat the transmission of that often more dangerous associate, heat. For example, cases have been known where a burning house has set fire to a timber fence over 60 yards away, notwithstanding that the wind was blowing in the opposite direction. It is true that flame is the actual igniting agent; but it can only produce this effect when the substance on which it acts has first been raised to igniting point by the influence of radiant heat, which may extend to distances beyond the reach of the flame itself.

This phenomenon of the distribution of heat, which constitutes the determinative factor in the spread of fire, should be combated as far as possible by the erection of protecting walls.

Assuming that the seat of a fierce conflagration is surrounded on three sides by protecting walls, of metal, stone, and wood respectively, behind which sundry inflammable materials are stored, it will be found in the majority of cases that those in the rear of the metal wall will be the first to take fire, then those behind the stone, and finally those protected by the wooden partition.

Similar results will be observed when three rooms, supported respectively by pillars of metal, stone (granite, limestone, or sandstone), and wood, are on fire. The one supported by the metal pillars will usually be the first to fall in, then that above the stone pillars, and last of all the one supported by the timbers.

According to a communication from S. H. Neissen, an oaken pillar, 10 inches square, resisted the action of a strong fire for thirty hours, and even then was only charred to a depth of 4 inches by 5. Under similar conditions, an iron pillar would have bent, and given way under its load. With regard to this property of wood, its low conductivity for heat, the insecurity of granite (cracking), limestone (falling to powder), and sandstone (splitting), the most important particulars have already been mentioned in treating of security against fire.

Under certain circumstances, wood must be credited with affording greater security against fire than either stone or metal, so far as the protection of inflammable substances from the action of heat is concerned, and also as regards its bearing strength—determined by the fact that it does not alter its position, or bend like iron under the same conditions.

From another point of view, however, wood exhibits a certain weakness that is not shared by iron or metal, namely, the tendency to ignite spontaneously when exposed to the protracted influence of a source of small external heat. At the same time, it is due to the wood to explain that this tendency is mainly the result of foreign substances introduced into it by nature, or applied by the hand of man. This proneness to spontaneous ignition can easily be diminished by suitable precautions and remedies, and the wood rendered quite flameproof by appropriate treatment.

This peculiarity is also exhibited by all other organic substances, the general law being that these are more endangered by gentle heat, provided the exposure thereto be prolonged, than by a powerful flame and high temperature. A certain protection against further combustion is, however, accorded to these organic substances by the fact that they char superficially, and thus part with their external layers of combustible matter, the residual carbon being difficult to consume except when supplied with oxygen by a powerful draught, a circumstance not very probable in the vitiated atmosphere of a fire.

Taking wood as typical of organic matter in general, and examining the reactions produced therein by the influence of heat, we find:—

All air-dry organic substances exhibit a tendency to firmly retain within their pores a certain amount of moisture, their “natural moisture,” which varies considerably, the limits ranging from 1 to 25 per cent.

When this moisture has been expelled by heat, and the substances have cooled down again, they will endeavour to reabsorb the same amount of moisture from the air. On prolonging the exposure to heat, without increasing the temperature beyond the point just necessary to drive out all the moisture ( $80^{\circ}$ – $105^{\circ}$ – $110^{\circ}$  C. usually suffices), the dried material, the main substance of which remains unchanged, sustains under the protracted influence of the heat a certain amount of alteration in its subordinate constituents, *e.g.* in the case of wood, the resinous matters, dried sap constituents, and applied paint; in the case of textiles, hair, or fibres, the fat and oil; in coal, the sulphur compounds and bitumen; in paper, the size, dressing, &c. Later on, the alteration becomes apparent externally, commencing with a slight browning, which gradually develops into charring, accompanied by the formation of gaseous products like carbon dioxide, carbon

monoxide, and hydrocarbons of various kinds, the material itself becoming richer in carbon.

The carbon formed in this manner does not remain the same, physically and chemically, throughout the whole series of stages, but undergoes progressive alteration, in the manner described below:—

When the heat applied does not exceed  $110^{\circ}\text{C.}$ , the water and most volatile aromatic constituents are expelled;

Up to  $150^{\circ}\text{C.}$ , carbon dioxide, carbon monoxide, and hydrocarbon gases are disengaged, and the resinous matters, sap constituents, &c., sustain considerable modification;

Up to  $230^{\circ}\text{C.}$ , external browning commences;

Up to  $270^{\circ}\text{C.}$ , self-lighting pyrophoric carbon is formed; followed, up to  $300^{\circ}\text{C.}$ , by the production of charcoal.

One stage in this series is attended with considerable risk of spontaneous ignition of the materials, although still far remote from the ignition point; and that is the moment the pyrophoric carbon is formed, at  $230^{\circ}$ – $270^{\circ}\text{C.}$ , this carbon having the property, especially when in the nascent state and for a short time afterwards, of taking fire in presence of warm air (*e.g.* from a lamp).

Pyrophoric carbon is also formed in other ways, for instance, when wood is exposed to high pressure in heated moulds, at a temperature approaching red heat, such as happens in making various kinds of toys, ornaments, beadings, furniture, &c. Under these circumstances the wood readily takes fire on exposure to the air whilst still hot, especially when the wood itself is resinous. Moreover, explosive vapours are liberated, with considerable noise, while the wood is being pressed.

In manufacturing operations, frequent opportunities arise for the formation of pyrophoric carbon and the occurrence of spontaneous ignition: a lamp hanging too near a beam; a steam pipe or hot air pipe laid too close to woodwork; dust settling down in thick layers on heated vessels or pipes; defective insulating material round a steam pipe, stove, fireplace, drying plant, &c., which are thereby enabled to radiate heat continuously against wooden articles—all these possibilities may occur in any factory, and, under favourable conditions, often lead to very perplexing outbreaks of fire.

High temperatures are unnecessary, steam under a pressure of 2–5 atmos., equivalent to a temperature of  $120^{\circ}$ – $150^{\circ}\text{C.}$ , being sufficient, the only essential being prolonged action. The same applies also to any hanging lamp

If the action is suspended for some time, and the heat comes into play only at intervals, this does not eliminate the danger, but merely delays its occurrence for the time being. The phenomenon of spontaneous ignition proceeds in the following manner (see also *Wood Charcoal, Gas Absorption*).

Heat when sufficiently prolonged, renders organic matter (wood) porous, whereby the wood is enabled to manifest the tendency possessed by all porous substances, namely, to absorb and attract gases. Now, the only gas available under the circumstances is air; but a selective affinity is exerted on the two constituents of the air, the oxygen being occluded more readily than the nitrogen, so that the porous wood becomes charged with air in which oxygen predominates.

Dried wood is able to take up a large quantity of gas: about 30-90 times its own bulk; and as soon as the action of heat recommences, the by no means small accumulation of oxygen in the pores greatly favours the production of pyrophoric carbon.

When this alternation of heating and gas absorption is continued for some time, a temperature of 270° C. is no longer essential to the production of pyrophorous carbon, 150° C. being sufficient under these circumstances; and in presence of occluded oxygen the carbon quickly takes fire.

From the foregoing it is evident that, in order to ensure safety in establishments that may be endangered by such moderate temperatures as those mentioned, it becomes necessary to some extent to remove all organic substances to a sufficient distance from all sources of heat, the distances varying from 2 to 4 feet according to the temperature developed. Similarly, care should be taken to prevent or remove any accumulation of dust on articles that radiate heat.

The best means of preventing the spontaneous ignition of organic substances at low temperature is by impregnation (*q.v.*). Merely superficial impregnation, however, affords only a temporary protection from the attacks of flame or sparks, and is powerless against the influence of even moderate warmth, the latter acting not merely on the surface, like sparks or flame, but gradually affecting the interior of the wood or other organic matter in question. The sole means of affording permanent protection is to thoroughly permeate the substance with antipyrenes, the power of organic substances to resist fire increasing with the thickness of the impregnated strata, and being incomplete until the latter extends right through.

The industrial branch engaged in the impregnation of organic substances, wood especially, is on the right track for solving this problem completely; experiments with fireproofed wood have shown that the same is capable of standing exposure to a temperature of 540° C. for twenty minutes without sustaining any appreciable alteration.

It may be remarked that the term "fireproof" currently used in this branch is scientifically incorrect, "flameproof" being the proper word.

In addition to being an almost indestructible protection against the spread of flame, properly impregnated wood is also the best insulator for preventing the dissemination of heat. A partition of impregnated wood exposed in a test fire so that the side next the fire attained a temperature sufficient to raise iron and stone to incandescence, registered a temperature of only 77° F. on the opposite side; the internal temperature of an impregnated wooden hut, completely enveloped by fire, was only 92½° F., and window glass protected by impregnated wood remained uninjured right through the experiment. These three facts can be confirmed by the author from his own observations of test fires.

Staircases of impregnated timber have proved equal to the best fireproof stone stairs in burning buildings.

The following conclusions were drawn by the author from his observations made in connection with a test fire in two huts, one constructed of so-called fireproof wood, the other of unimpregnated timber:—

1. The so-called fireproof wood is merely flameproof, and is partly destroyed by the action of fire, but is unflammable and does not spread flame.

2. The permeability by heat is exceedingly low, and hence impregnated timber is able to protect even very readily inflammable substances against the injurious effects of heat.

3. The presence of an unimpregnated core in the wood will considerably diminish its flameproof qualities.

4. Before insuring articles of alleged flameproof wood, care must be taken to ascertain that the impregnation is thorough and complete.

5. The general employment of thoroughly impregnated timber for building purposes and the manufacture of flameproof articles should be welcomed and advocated, such wood affording greater security than many alleged fireproof metal and stone materials, especially in preventing the transmission of heat.

The process of impregnating wood is attended with the same dangers as the drying of timber. In order that the impregnating materials may thoroughly penetrate the interior, the wood must be freed from water, sap, and air, a result unattainable without the employment of high temperatures. Where this can be effected by means of steam, the risks of drying by direct fire heat are mostly obviated; the temperature requisite in steam drying is about  $140^{\circ}$ – $160^{\circ}$  C. ( $284^{\circ}$ – $320^{\circ}$  F.), which corresponds to 6 atmospheres pressure.

The drying of organic substances and timber for building and working purposes is not unattended with risk, even in well-equipped steam plant. The articles must be properly arranged in the drying chambers and kept out of contact with the heating pipes. All openings in these pipes must be grated, and all dust must be cleared away from the pipes in good time, since if left to accumulate in thick layers it forms a readily inflammable mass with a tendency to ignite spontaneously. Great care should be exercised in drying highly resinous timber, the resin being liable to char as low as  $176^{\circ}$  F.; the temperature should be carefully watched, by the aid of thermometers that can be read from the outside of the drying chamber.

The best preventive of danger in these drying establishments is efficient ventilation and a careful supervision of the charge, the amount of heat supplied, and not the height of the temperature, producing the greatest drying effect. Hence, the operation of drying, unless controlled with great accuracy, is technically and economically erroneous, as well as being risky.

The best temperatures, in conjunction with abundant ventilation, are as follow:  $123^{\circ}$  F. for wood;  $64^{\circ}$ – $68^{\circ}$  F. for glue;  $77^{\circ}$ – $95^{\circ}$  F. for fresh plants or drugs;  $95^{\circ}$  F. for soap;  $86^{\circ}$ – $122^{\circ}$  F. for pharmaceutical preparations, and  $68^{\circ}$  F. for leather.

The duration of the process depends largely on the form and moisture of the mass under treatment; for thin wood, 10–12 days are required, and up to 30 days for thicker timbers.

The superficial impregnation of wood and organic substances is really no impregnation at all, but merely painting with antipyrrenes; and if inflammable materials, such as tar, tar oils, and the like, be used for this purpose, the protection afforded is rather against decay than fire. In fact, the inflammable character and capacity of the wood for transmitting flame are considerably enhanced by such treatment.

For these reasons, wood that is alleged to be impregnated should be carefully examined, to ascertain whether this impregnation is for

affording protection against fire or decay. In no case should the former condition be taken for granted.

That in some trades even explosive wood may be met with is demonstrated by the following instance. Staves from an old barrel that had served for storing the antiseptic and germicide known as antinonin, were found to explode with a violent outburst of flame when consumed as fuel under a boiler. They were evidently impregnated with this substance, which contains nitro-compounds. Similar explosions and outbursts of flame may be produced by all old casks, cases, &c., that have served for the conveyance of chlorates, nitrates, picrates, and such like compounds, firework charges, Bengal lights, nitro-compounds, gunpowder, &c.

### 3. Dyewoods, Sawdust, &c.

The various woods used for dyeing (logwood, Campeachy wood, redwood, Pernambuco wood, &c.) are subjected to fermentation in order to liberate the dyeing principles (hæmatoxylin, brasiline, santalin, from santal-wood). The chips are sprinkled with glue-water, piled in heaps, and left to ferment fourteen days, the operation, which is accompanied with the liberation of considerable heat, being carefully watched, so that it may not degenerate into charring and spontaneous ignition. The heating tendency is enhanced by the addition of urine and lyes, which are generally used. Similar behaviour is exhibited by sawdust and wood wool, if piled up in heaps whilst in a damp state.

In this case, however, another important factor comes into play; in the case of damp sawdust, the usual heating may be accompanied by putrefaction, not infrequently attended with the liberation of inflammable liquid phosphuretted hydrogen. Even should the two less dangerous (the solid or the gaseous) of the three possible compounds of phosphorus with hydrogen be present, the risk of spontaneous ignition is not entirely precluded, the decay of wood being often accompanied by the formation of nitrous acid, which converts the two harmless phosphides into the spontaneously inflammable liquid form.

These reactions occur wherever sawdust or wood wool is used as litter (stalls, foldyards) (see *Manures*), or exposed to rain or water during storage.

Sawdust from young or sappy wood (30–45 per cent. of moisture) is more liable to take fire of its own accord than that from older wood containing only 12–18 per cent. of water. Owing to the difficulty of estimating the percentage of water in sawdust or wood wool macroscopically, it is advisable to lay down the following precautions for all cases where sawdust is stored in bulk, or wood wool in a tightly packed condition.

The heaps must not be more than 7 feet high, nor may the materials be placed in contact with any wooden pillars, unless the latter have been impregnated in a thoroughly flameproof manner or protected by impregnated boarding. When used as litter, particular attention must be bestowed on the manure; that from sawdust litter must not be stored too long, or in high heaps, or it will be completely decomposed, with liberation of phosphuretted hydrogen. Strong nitric acid must not be allowed to gain access to either sawdust or wood wool, as even damp sawdust may be ignited by this acid. When incorporated with resinous materials in the manufacture of firelighters, sawdust may be induced to

take fire spontaneously if stored in large heaps; hence the lighters must be stored loosely, without any heavy pressure, especially whilst still hot when first made.

In admixture with blood, meal, glue, and gelatin, sawdust is converted into artificial wood by strong pressure; the temperatures employed in this operation may easily lead to spontaneous ignition, being  $340^{\circ}$ – $390^{\circ}$  F. An artificial wood, xylolith, is composed of intimately mixed wood fibre and mineral adjuncts; it is unflammable, incombustible, and can be used wherever fire is employed and stone or metal is unsuitable; *e.g.* for laboratory benches, chemists' shops, varnish works, drying frames, drying chambers, &c.

The very fine dust given off by wood when worked in lathes and other machines will explode on contact with any flame or spark, and thus cause great damage, especially when inflammable gases, like coal gas, are present. The originating cause of the dust is immaterial, every kind of wood furnishing explosive dust, even decayed wood that crumbles down to a state of fine powder. In fact, decayed wood in general is a source of no little danger. For instance, should a decayed beam become incapable of further supporting its load and collapse, the fine dust thus disseminated through the air of a room will ignite in contact with any light or fire present, and give rise to a violent explosion. It is rare that such ignition is produced by glowing bodies (cigars, pipes, ashes, slag), flame being necessary.

#### 4. Cellulose

The true and principal constituent of wood and many plants is cellulose (the substance of the vegetable cell). It occurs in its purest form in young plants, being strongly contaminated in older ones.

Cellulose appears in various forms: as long filaments it constitutes the textile fibres (flax, cotton, hemp, jute, nettle), and makes up about 30–50 per cent. of the substance of wood, straw, and esparto, from which it is extracted (as soda cellulose) by treating the raw materials with caustic soda lye under considerable pressure (10–14 atmos. =  $180^{\circ}$  C.), or as sulphite cellulose by means of calcium or magnesium bisulphite. A pure form is obtained by successively lixiviating textile fibres with ether, alcohol, water, acids, alkalis, and hydrofluoric acid. The application of the first three named materials on the large scale is attended with danger (see *Ether*).

Chemically pure filter paper and pure cotton may be cited as examples of pure cellulose.

The preparation of soda cellulose is dangerous, owing to the high temperature and pressure ( $195^{\circ}$  C. and 14 atmos.) involved; furthermore, the boiling of the wood, straw, &c., liberates combustible vapours, the chief constituent of which is often turpentine (*q.v.*).

The spent soda lye, being valuable, is often concentrated and calcined, whereupon combustible resinous vapours are also disengaged.

The sulphite cellulose process entails the preparation of calcium bisulphite, by burning sulphur or roasting pyrites (*q.v.*), and allowing the sulphur dioxide to act on limestone. These roasting operations are attended with risk.

The resulting sulphite solution is boiled with the raw material (disintegrated wood, straw, esparto, jute, &c.) in sulphite pans, at  $108^{\circ}$ – $118^{\circ}$  C.

(226°–244° F.), and sometimes also under a pressure of 5–6 atmos. Some risk arises in this process from the corrosion of the pan by the acid vapours, the vessel then easily bursting under pressure. For protection the pans are lined with lead or firebrick composition (Wenzel's); nevertheless they should be frequently tested as a matter of urgent necessity.

The spent sulphite lye is of value for the sulphur it contains, and is therefore concentrated and subjected to dry distillation. This treatment furnishes a good deal of inflammable gas, containing sulphuretted hydrogen (*q.v.*). As experiments with sulphite lye residues have led to explosions, it is essential that the sulphuretted hydrogen should be rendered harmless, either by burning or leading it away to some spot where there is no danger of fire.

Cellulose, which is itself quite free from risk, yields numerous preparations. With potassium and carbon disulphide vapour (*i.e.* a dangerous process) it forms cellulose xanthogenate, which acts as a substitute for glue, collodion, celluloid, and the waterproofing of fabrics. The product is quite safe, and when heated to 176°–212° F., gives a horny mass that is perfectly free from danger, and is suitable for replacing the readily inflammable celluloid. With glacial acetic acid, cellulose furnishes a perfectly safe substitute for collodion (cellulose tetracetate).

The innocuous character of cellulose is entirely changed when it is nitrated to nitro-cellulose (*q.v.*).

## CHAPTER XXXI

### LEATHER, GLUE

#### 1. Leather

THE dangers of leather-making are but small, the only objectionable point being the spontaneous heating (extending even as far as charring) of the tanned hides when piled into heaps. This autocarbonisation has been observed in the case of sheepskins tanned with sumach. Leather itself burns with difficulty, requiring a strong draught, and its vapours have an extinctive rather than a stimulative effect on flame.

The most important temperatures in tanning are in the sweating room, 78°–122° F.; warming the hides for greasing, up to 122° F.; heat in the dung pickle, 95° F. (the temperature here may, however, become higher). The lacquer varnish for application to leather is warmed up to 122° F., and is in itself a dangerous material.

The most dangerous process of tanning is that of tawing and chamoying (Morocco leather). The hides are well oiled or brushed over with train oil, and then piled in heaps, to undergo a process of fermentation, consisting in an oxidation of the fat. As is the case with fibres impregnated with oil, this operation may be and is accompanied by a considerable degree of spontaneous heating.

The process entails careful attention to prevent the hides from

charring of themselves, the danger is, however, less than in Turkey red dyeing, since the hides are more resistant towards heat than cotton.

The following materials may be mentioned as liable to exhibit objectionable features:—

Tan, which may become heated to the point of charring if piled in heaps in the warm while damp. Floating tan dust will ignite at an open light, fire, or in contact with sparks, and may even give rise to explosions (tan mills).

Quicklime (*q.v.*) must be kept at a distance from any inflammable substances, and be well protected from the wet.

Sodium sulphide (*q.v.*)

Wood vinegar in the plumping soak.

Oily and fatty waste, hairs, bristles. These must be kept properly stored, and only mixed with lime under special precautions (see *Manures, Calcium*). To ensure more thorough extraction of the grease, the raw or tanned hides are treated with benzol and alcohol, which treatment furnishes a more workable skin. In such tanneries, all the precautions appropriate to these two inflammable solvents must be adopted.

The haphazard mingling of the various tanning agents should be avoided as far as possible; oily or fatty substances should never be brought into contact with sodium sulphide, lime with tan, hair, or hide waste, but the different substances should be stored apart.

## 2. Glue

The manufacture of glue is frequently an important supplementary branch of the tanning industry. Glue can be recovered from leather scraps, bones, fish residue, feet, sinews, &c., a treatment with quicklime (*q.v.*) or sulphurous acid being required. The latter reagent may be prepared by burning sulphur, or purchased in the liquid form in explosion-proof steel cylinders. Under the latter circumstances all the precautions laid down for liquefied gases should be observed with care (see *Danger of Explosion*).

The boiling of the glue stock is occasionally effected at a temperature of 302° F., under a pressure of 4–5 atmos.

The drying of the glue is a safe operation, low temperatures being sufficient; in this event, however, a strong circulation of the air must be maintained, the maximum temperature at the heating surface being 300° F.

Glue burns only with great difficulty, and the resulting vapours quench fire.

## CHAPTER XXXII

### CHARCOAL

WHERE no particular kind of carbon is specified, the following particulars apply to all varieties of charcoal and the like, no matter of what origin.

The fundamental constituent of all kinds of charcoal, bone black,

wood charcoal, blood charcoal, lampblack, &c., is carbon, a substance exhibiting the widest possible differences in external appearance. Thus wood charcoal and the diamond are chemically identical, both consisting of carbon. The fusing point is  $3600^{\circ}\text{C}$ .

Every form of charcoal or substance consisting principally of that body possesses special properties, and behaves differently in respect of fire risk. Hence every variety must be dealt with separately, and at the same time we must not omit to mention the properties they share in common, wherever the same are most characteristically manifested. It should also be remarked that, whilst amorphous carbon burns at  $370^{\circ}$ – $375^{\circ}\text{C}$ ., the artificial graphite produced in the electric furnace will not do so below  $660^{\circ}\text{C}$ .

### 1. Wood Charcoal

This is the most important variety of charcoal, in the pyrochemical sense at least, and, as wood is regarded as the chief representative of the organic substances, so wood charcoal may be accepted as the principal type of charcoals in general.

The charcoal industry has grown considerably in importance. Formerly the sole method of preparation consisted in charring wood in heaps (charcoal pits), an operation attended with little risk; but at the present time large furnace and retort plant is employed, which is of such excellent construction that gross carelessness alone can lead to the violent explosions to which the process is liable.

The wood is carbonised at  $300^{\circ}$ ,  $500^{\circ}$ , and even up to  $1000^{\circ}$  and  $1500^{\circ}\text{C}$ . according as charcoal or the volatile matters of the wood form the main object of the process. The operation is one of dry distillation, the wood being heated with wood or coal fuel, superheated steam, blast-furnace gas, or hot air.

As in all processes of making charcoal, the main point to be observed is that only a little air, or air poor in oxygen, is admitted to the charring furnaces or retorts, since otherwise an explosive mixture would be formed with the wood gases; this latter, in fact, constitutes the chief danger of these processes. In some cases the wood is subjected beforehand to heavy pressure (up to 1500 atmos.) to free it from water.

The first distillation products in charcoal-making are explosive gases and vapours, hydrogen, benzol vapours; then follow creosote, acetic acid, wood spirit, paraffin, and ammonia (see *Tar, Wood Tar*).

The residual charcoal may be fiery or safe, according to the process employed and the age of the product. Old, air-dry charcoal that has not yet been ground, worked, calcined, or mixed with certain other substances (see later) is free from all danger.

So soon, however, as anything is done with the charcoal, *i.e.* it is worked, warmed, dried, pulverised, moistened, rubbed, or mixed with other substances, the nature of the charcoal is altered; and indeed, by certain treatment, it can be converted from a harmless substance into a dangerous one capable of self-ignition. The alterations have some connection with the porosity of the charcoal.

When suffused with fuming nitric acid, charcoal develops very great heat, which is attributable to a nitration of the subordinate constituents or an oxidation of the carbon (eventually spontaneous ignition) may ensue.

## 2. The Occlusion of Gases by Charcoal

Just as a sponge absorbs water, so the innumerable pores of all kinds of charcoal possess an extraordinary affinity for moisture, gases, and vapours. According to Joulin, 4 grams of charcoal at zero C. will absorb :—

47 cc. of nitrogen, or 216 cc. of carbon dioxide, or 129 cc. of oxygen, or 548 cc. of ammonia gas.

According to Saussure, boxwood charcoal will absorb :—

Oxygen . . . . .	9-14 times its own volume.
Carbon monoxide . . . . .	9       "       "
Marsh gas . . . . .	35       "       "
Carbon dioxide . . . . .	35       "       "
Sulphuretted hydrogen . . . . .	55       "       "
Sulphur dioxide . . . . .	55       "       "
Ammonia gas . . . . .	90       "       "

The operation is complete in 24-36 hours, and then ceases; only in the case of oxygen does the absorption proceed further, and may extend over an entire year, by the end of which time the absorbed gas amounts to 14 times the volume of the charcoal, without having attained finality even then.

The affinity for absorbing gases may be increased by diminishing the air pressure; boxwood charcoal, for instance, that under 760 mm. pressure takes up 34-35 times its own volume of carbon dioxide, being able to occlude 69 times under a pressure of 260 mm.

On the other hand, this capacity is considerably impaired by the presence of moisture.

Each kind of charcoal exhibits a special affinity for certain gases, wood charcoal taking up a larger amount of hydrogen than any other species of charcoal.

The dimensions of the pores constitute a measure of the absorptive capacity, the larger the pores the smaller the amount of gas absorbed per cent. If, however, the pores be infinitely minute, the absorption again suffers diminution.

Cork and sugar furnish a frothy charcoal with large pores and absorbing only a small amount of gas; pine charcoal is also coarse in the pores in comparison with that from boxwood, which is able to absorb twice as much gas as the first-named.

If charcoal that is fully charged with one kind of gas be immersed in another gas which it would otherwise absorb, this second gas displaces a certain proportion of the first one, the amount depending on the affinity of the charcoal towards the second gas.

When a mixture of several gases is placed at the disposal of the charcoal, the absorption will take place in accordance with the relative affinity of the charcoal for the several constituents of the mixture. The result will be the same as though the gases were presented separately, except that, in the case of certain gases, the total amount absorbed is greater than that of the individual gases. Thus, for instance, charcoal will take up more from mixtures of oxygen and hydrogen, oxygen and

carbon dioxide, oxygen and sulphuretted hydrogen, than it will of the same gases offered separately.

On the other hand, the absorption is reduced in the case of mixtures of carbon dioxide and hydrogen, or carbon dioxide and sulphuretted hydrogen.

On the basis of these facts, which have been demonstrated by experiment, the following remarks may be made in connection with charcoal and its absorptive capacity for gases:—

(a) Gas mixtures containing oxygen are absorbed in greater quantity than the several gases, or mixtures, free from oxygen.

(b) Gases that can readily be condensed to liquids at the ordinary temperature (true vapours) are occluded in far larger amount than the true gases which entail the application of very low temperatures and high pressure for their liquefaction.

(c) Accordingly, charcoal will absorb more alcohol, ether, water, sulphur, and hydrocarbon vapour than oxygen, hydrogen, carbon dioxide, carbon monoxide, or sulphuretted hydrogen.

(d) Moist gases and vapours are absorbed more greedily and retained more tenaciously than when dry.

Although the foregoing remarks would appear to have but little connection with the fire risk of charcoal, they had to be introduced here because the risk in question depends not merely on the actual mass, its composition and origin, but also, and principally, on its capacity of absorbing liquid or gaseous substances into its pores. Hence it is the occluded gas in charcoal, and not the carbon thereof, that mainly determines the degree of fire risk exhibited by that substance.

We are now in a position to understand charcoal and its relation to danger from fire.

Newly made charcoal, and such as is still in a semi-incandescent condition, has not had time to occupy itself with the absorption of appropriate substances, liquid and gaseous; its pores are still empty, everything having been expelled therefrom by the heat. Such charcoal, with its empty pores, is in the most dangerous condition possible. In the necessity for satisfying its natural tendency to absorb material to fill the pores, it takes up whatever happens to be nearest. If this be a gas, then condensation occurs in the pores, a phenomenon always attended with liberation of heat (see *Spontaneous Heating*, *Spontaneous Ignition*); if liquid or solid bodies, like pigments or scents, the liberation of heat is inappreciable, or else the heat is absorbed by the liquid itself, and its effects do not become manifest.

On the other hand, in the case of gases, this disengagement of heat may attain such an altitude that the charcoal becomes hot and incandescent, or even takes fire spontaneously.

### 3. Spontaneous Ignition

The risk of this phenomenon occurring is the greater in proportion as the charcoal is freshly made, and the hotter it is at the time of its exposure to the air. The danger disappears in the course of 2–3 days; if the charcoal be meanwhile kept away from air, and only exposed thereto when thoroughly cool, the absorption of gas proceeds but gradually. This precaution should be adopted in all cases, being essential to safety.

Old charcoal will attain the same danger as is manifested in this respect by that newly prepared, if it be heated up again, the heat expelling the occluded gases and revivifying the absorptive power (regenerating charcoal for bleaching or disinfecting purposes).

In the opinion of many, the absorptive power of charcoal that has been frequently used and regenerated by heating, is increased, and hence old charcoal should be more liable to ignite spontaneously. It is, however, unnecessary to reheat safe charcoal in order that this property may be acquired, a simple pulverisation being sufficient for that purpose, if the charcoal is not already in a state of fine powder. The manner in which pulverisation is effected (grinding in mortars, ball mills, falling, shaking, during transport, &c.) is immaterial, the result being the same, viz. to open the pores that have hitherto been closed, and thus increase their number. Practical experience has shown that this is frequently sufficient to restore the tendency to ignite spontaneously.

This same tendency also exists in freshly powdered charcoal, but only for 2-3 days, during which time it must be kept away from the air, or from gases or vapours; afterwards there is no danger. Similar behaviour is exhibited by carbonised peat.

When freshly powdered, charcoal will not stand tight packing; experiments have shown that such charcoal, when packed close in casks, attains a temperature of 75° C. in five hours, and will take fire in five hours more.

Moistening charcoal will powerfully stimulate the tendency of charcoal to take fire spontaneously, after re-drying. In this case the moisture expels the occluded gases just as is effected by heating to incandescence. So long as the liquid occupies the pores the charcoal is safe, until it evaporates on drying and leaves the pores again empty.

Comparative tests have demonstrated that such charcoal, when re-dried, will shortly take fire, at a temperature below 250° C.

Fats and oils also play a dangerous part in charcoal, the pores of which extend these substances over a large superficial area, in the same way as is done by fibrous materials. Greasy charcoal may easily ignite of its own accord.

From the foregoing it will be clear that any treatment that frees the pores of charcoal from occluded gases and vapours may produce spontaneous ignition. Even the simple storage of new or old charcoal in large heaps is attended with danger of the same result. Temperature readings taken in heaps of lump charcoal, measuring about 32 square feet in area and 5-6 feet deep, gave the following results: First day, 57° F.; second, 89° F.; sixth, 149° F., the heap taking fire on the thirteenth day.

The succession of these stages is the more rapid in proportion as the charcoal is in a more finely divided state. For this reason finely powdered charcoal should always be stored in small heaps at first and kept dry, the size of the heaps being only increased when the shape of the charcoal permits of an active circulation of cooling air. Knots in large lumps of charcoal may remain red hot for a considerable time, and thus lead to an outbreak of fire.

Should it be impossible to avoid storing the charcoal in large heaps, these must be shovelled over once a week to increase the superficial cooling of the mass.

It should be noted that the effect of subjecting charcoal to a vacuum

or attenuated air is to empty the pores in the same way as is done by heat or moisture; and that, when exposed to the air again, the charcoal greedily absorbs gases and becomes heated.

Solid substances, which, although apparently dry, give off moisture, and also liberate oxygen when gently heated (see *Carriers of Oxygen*), are just as dangerous to charcoal as are moisture and gases (oxygen in particular). Charcoal should not be stored or placed in contact with hygroscopic substances (calcium chloride, magnesium chloride), which, by their attraction for water and moisture, may saturate the charcoal with water; the same applies to metallic sulphides with an affinity for oxygen (see *Pyrites*), and to ozone, liquid oxygen, oil of turpentine, and all substances that readily part with oxygen.

New parcels of powdered or coarse charcoal should be handled with suspicion, since from some unknown cause (freshness, recalcination, drying, or moisture) they may contain the germ of a spontaneous outbreak of fire, still undetectable. During the first three days after arrival the goods must be stored in a fireproof manner, or else the internal temperature of the mass be controlled by frequent readings, since it is only after this time has elapsed that one can tell whether the tendency to spontaneous ignition really exists or not. These precautions are particularly necessary when the charcoal is tightly packed.

The minimum of risk from the foregoing causes is exhibited by charcoal that is rich in mineral constituents; such as bone-black, which largely consists of calcium phosphate.

"Prepared" (impregnated) charcoal, of course, no longer retains its fiery tendency, the pores being obstructed by the added material and remaining closed until the charcoal is burned.

These preparations include the blocks obtained by moulding charcoal powder in the warm along with saltpetre, tar, dextrin, paste, &c. They usually possess a high capacity for smouldering, and are used for calcining, ironing, and for heating Nieske charcoal stoves, foot-warmers, railway carriages, &c. The combustion proceeds without flame, being restricted to a quiet, almost imperceptible glimmer.

Electrical carbon must also be regarded as a prepared charcoal. To this class belong the carbon pencils for arc lamps, carbon for galvanic batteries, carbons for lightning conductors (telegraph apparatus), and electrode carbons for the electric furnace.

Electrical carbon is prepared from charcoal, ground very fine, mixed with tar, and heated to 1000° C. in circular furnaces by means of generator gas. The tar at first gives off explosive vapours; and the grinding and treatment of this charcoal also entails care, though it is far less dangerous than ordinary charcoal. For certain purposes, electrical carbon has to be impregnated with paraffin or shellac, an operation not unattended with risk; an example of this is afforded by the carbon for electric batteries, impregnated to prevent the acid penetrating too quickly into the carbon.

#### 4. Lampblack

Lampblack is prepared in various ways, and is known by different terms in accordance with its origin: gas black, ivory black, Frankfurt black, oil black, printer's black, varnish black, gloss black, &c. It consists of finely divided carbon, which separates from the flame in flakes

during imperfect combustion; and of sundry subordinate substances, solid, liquid, and gaseous. Its composition depends on the method of preparation and the raw material, which latter may be: (a) wood, resin, tar, oils, the flame furnished by the imperfect combustion of which gives a lampblack contaminated with tarry, oily, empyreumatic substances; (b) colophony, camphor, camphor oils, acetylene, benzol, and hydrocarbons generally—these yield, on incomplete combustion, an almost pure lampblack, which can easily be freed from its subordinate constituents (gases and liquids) by repeated heating to redness, and then consists of almost pure carbon.

Lampblack-making is often a supplementary industry, though some factories are occupied with this work exclusively and turn out a particularly fine product. In the former case the soot from the furnaces is collected in special cool chambers; but in the other, the raw material is burned as slowly as possible, in lamps if liquid, and in pans if solid, the flame and smoke being passed through flues into cold chambers, where the lampblack is deposited; or the flame is allowed to impinge on rotary, water-cooled hollow cylinders, from which the deposited black is removed by stationary brushes.

Recently, a fine grade of lampblack has also been prepared from acetylene, a process that is dangerous inasmuch as the acetylene used is under a pressure of 2–3 atmos. and is ignited by electric sparks (see *Acetylene*).

The other processes are attended with danger, though not in such a high degree as the last-named. Where lampblack is produced by passing an electric current through a hydrocarbon, which is thereby decomposed with some violence, the occurrence of short-circuiting, by the adherence of solid particles of carbon on the electrodes, is not impossible. Again, the method wherein gaseous hydrocarbons are passed through red-hot pipes is exposed to considerable risk of vapour explosions.

It may be taken as a general axiom for the lampblack industry that the more complete the installation, the purer the raw materials, and the better the control over the air supply and the removal of the gas and vapours the smaller the danger, which in these works is mainly one of explosion. At the same time the works are liable to disturbances, which then play a dangerous rôle.

The danger is greater in works where lampblack is recovered as a bye-product, or where it is produced by accident. This latter event is liable to occur in premises where the charring of organic materials is practised, *e.g.* cork, husks, straw, leather, waste of all kinds, rags, grape skins, tan, oils, &c., and where the object of the process is the production of Spanish black (*q.v.*), or the like rather than lampblack. A dangerous formation of lampblack occurs in the domes of petroleum stills, which black manifests a keen tendency to spontaneous ignition when work is stopped and the stills are opened, *i.e.* on admission of air. According to the researches of R. Kissling, this black consists of carbon, 67 per cent.; iron, 24 per cent.; sulphur, 9 per cent. He rightly attributes the fiery nature of the black to the presence of the iron and sulphur, and he recommends, in view of the danger of explosion arising from the presence of the black in the readily inflammable and explosive oil vapours, that some arrangement should be devised for preventing the deposition of the black so close to the inflammable oil, *i.e.* not in the dome itself.

Experiment showed that even after the black had been extracted with boiling hydrochloric acid and water to remove the iron and sulphur, it still ignited at the relatively low temperature of  $150^{\circ}$  C. The best means of obviating this danger in the still is to see that there are no horizontal projections or ledges on which the deposit can occur in the dome.

It has also been demonstrated on numerous other occasions that the presence of iron and sulphur (*i.e.* iron sulphide) will render lampblack liable to take fire spontaneously. Should the raw materials contain these substances it may be concluded that they will not be absent from the product.

Tar, tar oils, mineral oils, coal, lignite, and peat all yield lampblack that is somewhat highly charged with sulphur and should be kept out of contact with iron. On the other hand, the black from fats, resins, and fatty oils contains but little sulphur, while the purest of all in this respect is furnished by the hydrocarbons, acetylene, benzol, and naphthalene. As, however, these latter substances are dearer, the others are mostly used, the crude black being purified by repeated extractions with acids and alkalis and recalcination.

In these recalcinations, air is alternately excluded and admitted, thus producing the dangerous condition (leading to spontaneous ignition) referred to under *Charcoal*. What has already been stated with regard to the latter substance under these circumstances, applies also to lampblack: the alternate deprivation of air (emptying the pores) by calcination, and subsequent readmission of this agent (occlusion of atmospheric oxygen), producing such an amount of heat as to lead the black to take fire. Lampblack possesses a greater power of retaining heat than any other form of carbon; hence the frequently surprising heating influence soot exerts on the soil when spread thereon as manure and exposed to the rays of the sun.

Very gradual cooling, and exclusion of air until cooling is complete, form the sole means of protecting freshly calcined lampblack from spontaneous ignition. It is dangerous to use lampblack until it has been stored for a few days and exposed to the air without taking fire.

As in the case of charcoal, the spontaneous ignition of lampblack is favoured by moisture (*e.g.* wet weather), moist oxygen being attracted more avidly than when dry.

The numerous industrial applications of lampblack frequently necessitate admixture with other materials. If the mixture be wet or damp, there is no danger, provided the ingredients themselves are of a harmless character; but where these substances are dry and are also carriers of oxygen, such as permanganates, chromates, chlorates, or peroxides (barium peroxide, manganese peroxide, or the liquid hydrogen peroxide), the oxygen may contribute to spontaneous ignition, the pure gas being absorbed with greater avidity than that in the atmosphere. A similar effect is produced by such substances (many metallic sulphides—iron sulphide in particular—and pyrophores) as attract oxygen from the air, though not containing any themselves.

An addition of fats or oils to lampblack will spoil it in the same way as with charcoal; and, given the right kind of oil and suitable conditions, small quantities will suffice to produce ignition, as in the case of greasy rags and oiled fibres.

Dust explosions are also liable to occur when lampblack is dissipated in the air of closed rooms during use. The explosion may be started by simple ignition at a light, sparks, or glowing bodies, and may also ensue spontaneously if the lampblack is in admixture with some inflammable gas or vapour (coal gas, vapour of benzol, ether, marsh gas). See *Dust Explosions* and *Coal Dust*. Where lampblack is used, every kind of illuminating or inflammable gas should be excluded.

Lampblack factories are particularly exposed to the risk of explosion, owing to the considerable quantities of unconsumed hydrocarbon gases adhering to the particles of lampblack and thus contributing to the explosibility of the mixture. These dangers can only be combated by stringent precautions.

Before recommencing work, a good current of air must be passed through the apparatus, black flues, and settling chamber, in order to clear away any residual explosive gaseous mixtures or dust. While work is in progress, all retorts and other vessels must be shut off from communication with air. Endeavours must be made to prevent the dispersion of the fine black during and after working hours; and rooms containing floating dust must not be visited with naked lights, all illumination being effected from the outside, or with properly closed lamps.

Lampblack must not be packed as soon as made, since any tiny spark remaining unquenched therein may set fire to the entire stock. The black must be protected from damp, and from fatty substances. Any mixing of lampblack with substances likely to endanger it must be confined to isolated rooms (see above).

## 5. Spanish Black

This product is similar to lampblack, but, instead of being deposited from the flame of a burning substance, is obtained by the calcination of organic matters in closed retorts out of contact with air. Numerous raw materials are used: cork, grain husks, straw, hides, leather, bones, sinews, tendons, rags, grape skins, tan, peat, residues from the manufacture of potassium ferrocyanide, and other industrial and domestic refuse.

In all these materials, the waste products in particular, it is necessary to see that they are free from grease and oil; since, apart from the tendency to spontaneous ignition imparted by fat to fibres, textiles, &c., the fatty matter furnishes oil gas during the calcination process, which gas may form explosive mixtures with air and other gases.

The best way of obviating these explosions, which may also occur even when the raw materials are free from fat, is to preclude all access of air to the retorts, and thus prevent the formation of explosive gases. The risks are analogous to those incurred in gas works, but greater by reason of the less perfect equipment of the (often very primitive) lampblack factory.

Unlike lampblack, the crude product, instead of settling down in fine flakes, has to be ground, which augments the risk (see *Charcoal*), especially when the grinding (usually in ball mills) immediately follows the calcination; this revives the predisposition to ignite spontaneously, and the more so the moister the weather (see *Charcoal*).

In order to bring the black up to anything like the quality of lamp-

black, it must be ground extremely fine, and this operation in turn leads to the formation of floating dust liable to produce an explosion (see *Dust Explosions*).

In general the same precautionary measures must be laid down for Spanish black as for lampblack and charcoal.

## CHAPTER XXXIII

### COAL

#### 1. Spontaneous Ignition

UNDER the term coal we include all the kinds of carbon, as coal, lignite, briquettes, coke, and anthracite, used for fuel or gas making. Coke and anthracite will be mentioned specifically by name when they come in question; the dangers they give rise to are inconsiderable.

The chief risk attaching to coal in storage is the liability to spontaneous ignition, which, however, differs greatly according to the pit whence the coal is obtained, and the way it is handled.

Many of the dangers inherent in coal are referable to the extremely complex composition of the coal itself, among its constituents being: spontaneously inflammable pyrites; readily inflammable liquids, like benzol, ligroin, &c.; and the gases hydrogen, methane, and carbon monoxide, all of them forming explosive mixtures with air.

On all sides coal presents dangers of some kind: in its ordinary condition by spontaneous ignition and dust explosions; when decomposed into its various constituents it manifests the dangerous properties inherent in these latter.

There is no need to enumerate the various interesting cases of spontaneous ignition in coal, these the reader will find mentioned in L. Häpke's work on that subject, but our chief attention will be devoted to the causes of this phenomenon.

The opinions of experts on this question are still contradictory, a fact explainable by the great variety in the composition of coal and the different ways in which it is stored, transported, used, and treated.

The danger of spontaneous ignition in the coal store is present in every establishment; and after fifty years have elapsed without an accident of this kind, the fifty-first may witness three or four in succession.

It is impossible to decide which kind of coal is the most liable to this risk, no reliable information on the point being afforded by either test fires or the experience gained in practice. All that can be definitely said is that certain collieries usually furnish coal with a tendency to ignite spontaneously, while others do not; that certain coals which have not hitherto taken fire of their own accord may do so under certain circumstances; and that some coals generally considered fiery occasionally remain safe for long periods.

Coal from the Ruhr district of Germany is more liable to spontaneous ignition than that from the Saar coalfield, and lignite (brown coal of woody structure) is more fiery than other grades of brown coal. Some

experts favour the view—though quite as many are of the contrary opinion—that the amount of coal stored is the decisive factor for the occurrence of spontaneous ignition, for in the year 1874, out of 4494 ships laden with coal, outbreaks of fire occurred on :—

5 ships out of 2109 carrying		500 tons each	= $\frac{1}{4}$ per cent.
17	“	1510 “ 500–1000	“ = 1 “
17	“	“ 490 “ 1000–1500	“ = $3\frac{1}{2}$ “
14	“	“ 308 “ 1500–2000	“ = $4\frac{1}{4}$ “
7	“	“ 77 “ over 2000	“ = 9 “

According to these figures the danger of spontaneous ignition increases with the tonnage stored, and seemingly without reference to the origin of the coal. The length of the voyage, too, apparently has some influence on the risk, since in the above-mentioned year, out of 31,116 ships laden with coal, accidents by spontaneous ignition occurred on board 70, of which 10 were plying between British and continental ports, and 60 on the way to Asia, Africa, and America, *i.e.* remote destinations.

Other factors stated to influence spontaneous ignition in coal are: the presence of pyrites, moisture, the ventilation of the storage heaps, and the comminution of the coal in transit.

In view of the often contradictory facts that are as frequently disproved and again confirmed, it would be erroneous to ascribe all cases of spontaneous ignition in coal to any single cause. In fact, eleven different causes are known, and though it is unnecessary for all to act in concert, the occurrence of a spontaneous outbreak of fire from one of them alone is a rare event. Where four, six, or ten of these causes are naturally present in any coal, that coal may be said to possess a decidedly fiery tendency; but where only one, two, or three of them appear, the coal has little or no inclination to take fire of its own accord.

The causes themselves are in part inherent in the coal or make their first appearance when the coal is loaded, conveyed, and stored. Before proceeding to discuss these causes and their remedies mention must be made of the following particulars.

The critical temperature, or point at which the ignition of the coal is effected by heat, is in general as follows, for mixed lump and small coal :—

Lignite,	.	.	.	.	.	150° C.
Charcoal,	.	.	.	.	.	200° C.
Coke,	.	.	.	.	.	250° C.
Anthracite,	.	.	.	.	.	300° C.

Sources of danger in various ways to coal are violent *movement*, which grinds and pulverises the coal; moderate but persistent *warmth*, which liberates gases; *wet*, rain, &c.

The *presence* of certain substances, as carriers of oxygen, sulphur, sulphur compounds, fat, oil, &c.

The influence of *flame* and *fire*.

The various kinds of coal behave very differently in burning.

*Bituminous* or *caking coal* first softens, swelling and frothing up, and finally cakes to a homogeneous porous mass. This coal is rich in gas, is

the easiest of all coal to light, and burns with the greatest and longest flame.

*Clod coal* softens and cakes into a solid mass without frothing.

*Non-caking coal* neither softens nor changes its shape. It leaves a pulverulent residue when burned, is poor in gas, and is very difficult to kindle.

On the basis of numerous practical experiments, tests, and observations, the following causes of spontaneous ignition in coal have been determined:—

1. The presence of sulphur (as pyrites).
2. The presence of coal gases (marsh gas).
3. The absorption of oxygen by the coal.
4. Weathering.
5. Porosity.
6. The formation of dust.
7. Wet.
8. The application of heat (from 100° F. upward).
9. Defective ventilation, surface cooling.
10. Internal ventilation by the formation of cavities in the heaps.
11. The presence of pyrophoric, heat generating, extraneous substances.

**Presence of Pyrophoric Substances.**—Oily or greasy waste (rags, filter-materials, tow, wool, &c.) is present in every establishment containing machinery, and this dangerous material may gain access to the coal heaps, either by accident, carelessness, or the instrumentality of rats, mice, or cats. Where the coal is very dusty the danger of spontaneous ignition from this cause is imminent, and therefore the greatest care should be bestowed on the storage and treatment of all oily or greasy substances, however worthless, and the same should be thrown into the boiler fires daily.

**Weathering.**—As soon as coal is raised from the pit and exposed to the air it parts with its natural moisture; the surface cracks, and the pores open, atmospheric oxygen being thereby admitted to the interior of the lumps. In this manner the coal weathers and crumbles away, so that by the end of five weeks' storage as much as 40 per cent. of coarse dust may be formed. As will be seen, this dust is explosive and augments the risk of spontaneous ignition, the danger increasing with the fineness of the dust.

This weathering tendency may be successfully counteracted by blowing steam into the storage heaps, or by coating the lumps of coal with resin or coal-tar pitch; the resulting generation of heat, however, brings other dangers in its train.

Water has proved better than steam for temporarily retarding the crumbling and weathering of coal. All crumbly coal intended to be stored for any length of time should be damped superficially, but only just enough to prevent access of air, not wetted. When, however, strongly pyritic coal is in question, the damping process must be omitted, since moisture and pyrites in conjunction largely contribute to spontaneous ignition (see *Sulphur in Coal*).

**Applied Heat.**—Even moderate heat (85°–100° F.), when protracted, tends to decompose coal and favours spontaneous ignition, pyritic coal in particular suffering extensive decomposition.

Dangerous heat of this kind is supplied by steam, hot air, and hot water pipes, flues for the conveyance of heated vapours or gases, hot walls, remote sources of heat, stoves, and cinder heaps. Coal that is to be stored for any length of time must be situated at least 20 feet away from such dangerous objects.

**Sulphur and Metallic Sulphides in Coal.**—Coals exhibiting a yellow or whitish film of sulphur compounds are readily brought to ignite spontaneously by even a small amount of moisture. Chief among these sulphur-compounds is iron sulphide, which *per se* does not ignite below  $200^{\circ}\text{C.}$ , but, when in the extremely fine state of division in which it occurs in coal, is acted upon strongly by atmospheric oxygen (like oil disseminated in fibrous substances). As in all chemical processes, this reaction is attended with the liberation of no inconsiderable heat, and if this occurs in the interior of the heap, the retention of same by the mass of coal may produce dry distillation and ignition.

The accumulation of heat may easily generate a temperature of  $300^{\circ}\text{C.}$ , at which point spontaneous ignition begins. Should, by any chance, sulphuretted hydrogen gas be produced or used on the premises, and the coal have an opportunity of absorbing this gas, spontaneous ignition may occur, even at  $175^{\circ}\text{C.}$  ( $347^{\circ}\text{F.}$ ).

The dross and smalls from coal-washing plant are rich in sulphur compounds, and therefore particularly liable to take fire. When piled in heaps they rapidly grow hot, and therefore should not be used for packing the goaf. The best method of dealing with this waste is to gasify it in shaft furnaces, the heat of the glowing dross being utilised for warming the air supplied to the boiler fires.

**Methane in Coal.**—Freshly raised coal is charged with gas, formed at the same time as the coal itself, which gas constitutes the explosive mixture known as "fire-damp." The composition of the gas varies in different pits, but in all cases the bulk consists of methane and ethane.

The fresh coal, and especially lump coal, continues to give off this gas for some time. When the coal is stored in the open the danger is small; but if the heaps are very high, or the coal is tightly packed in enclosed spaces (ships' holds, bunkers, or cellars), and the escape of gas into the outer air is restricted, the gas will occupy the residual air-space in the place of storage; and in such event even the smallest flame or a hot spark will suffice to explode the mixed gas and air.

On long voyages the unavoidable rolling movement of the coal greatly assists the expulsion of the gas and the formation of an explosive mixture with air. Nevertheless, though dangerous in presence of an open flame, the gas is never a direct cause of spontaneous ignition in coal.

**Occlusion of Oxygen.**—During or after the liberation of methane, coal absorbs oxygen. By many this occlusion of oxygen is, perhaps rightly, considered to be the main cause of spontaneous ignition in coal. The quantity of oxygen taken up is considerable, and may attain up to 5 per cent. (of the weight of coal) in the case of anthracite, and up to 10 per cent. in lignite (see *Charcoal, Absorption of Gases*).

This occluded oxygen combines with the readily oxidisable constituents of the coal, and the resulting heat suffices to ignite the finer particles of the coal itself.

The rapidity of the oxygen absorption is accelerated uncommonly by fineness of division, and also by warmth. Coarser coal is able to take up just as much oxygen, only much more gradually; but, on the other hand, warm coal will absorb far more of the gas than in the cold state, and that, too, in a much shorter time. On this account the temperature of coal during storage should never exceed  $86^{\circ}\text{F.}$ ; should it rise to  $154^{\circ}\text{F.}$ , spontaneous ignition becomes merely a question of time, since coal charged with oxygen can easily be kindled at  $275^{\circ}\text{F.}$

**Coal Dust.**—Coal is most dangerous when disseminated in the form of floating dust, since, in this condition, the absorption of oxygen and its reaction on the coal, the affinity for extraneous gases, the oxidation of iron sulphide, pyrites, and the readily oxidisable coal constituents, all proceed with greater speed and energy; so much so indeed, that they may become manifest as explosions.

A separate section being devoted to dust explosions, it will be sufficient to briefly report here on those occasioned by coal dust.

## 2. Coal Dust Explosions

Formerly it was assumed that about 2 lbs. of coal dust per 35 cubic feet of air formed the quantity necessary for the production of an explosion, but experiment has shown that as little as one-third of an ounce (*i.e.*  $\frac{1}{100}$ th part the above quantity) will suffice, and that it is more a question of the fineness of division of the dust than the weight. When the dust is so impalpable as to be capable of floating for hours in the air, it even becomes liable to explode spontaneously. This danger of explosion is present in all places where the mechanical treatment of coal is carried on, especially in the production of lignite briquettes and the preparation of coal dust for fuel.

As in most dust explosions (*q.v.*), so here; the floating dust is first ignited by a flame, whereupon the resulting gases and vapours (carbon monoxide and hydrocarbons) mixing with the air, and the gaseous products adhering to the particles of coal dust, produce the actual explosion. We have therefore two stages to deal with, the preliminary ignition contributing its heat of combustion to the instantly succeeding explosion.

Firedamp explosions may occur above bank, in the coal-washing plant, as well as in the pit. When the slide of the fines tower is opened to discharge some of the contents, cavities may form within the mass of coal, just as they do through the hanging of the charge in the blast-furnace. As the superincumbent mass drops, the internal air, which is more or less laden with methane, is driven violently out through the damper door; and, should the air in question come in contact with an open flame or fire, it is but rarely that an explosion fails to ensue. True, the percentage of methane in the air from the tower is very low (only 1–2 per cent.), but in association with coal dust, even this small amount is sufficient to render the air explosive. In such cases, good safety-lamps should alone be used.

The danger of coal dust explosions exists only so long as the dust is suspended in the air, and ceases as soon as the latter settles down; to reappear, however, when the dust is stirred up and set floating again.

The maximum danger is attained when the formation of clouds of

dust is oftentimes repeated, since they are most particularly sensitive to ignition, from any cause, in their nascent state. Moreover, this frequent resuscitation of coal dust clouds gives rise to certain other dangers, the dust forming a deposit on all objects and in all accessible places in the vicinity: steam pipes, pipes for hot liquids or gases, or spots contaminated with oil, fat, or lubricating materials; in fact, all places where incrustations of coal dust are gradually formed, these being exceedingly inflammable, and where fats or oils are in question a high tendency to spontaneous ignition may be induced.

Such incrustations on hot pipes are easily ignited by the radiant heat liberated from the latter; and the spontaneous ignition of the greasy particles of coal is merely a question of time.

It is fairly certain that numerous outbreaks of fire are due to the year-long accumulation of thick incrustations of coal dust. The cause of such paradoxical fires is never ascertained, this particular point being overlooked.

A few drops of oil let fall from a lamp on to an incrustation of this kind will be sufficient to impart pyrophoric tendencies to the portions touched. The same cause will also endanger the insulating lagging on the steam pipes, this lagging being powerless against the action of pyrophoric substances, though capable of standing the heat of the pipes. In one instance smouldering was detected in an insulating material containing as much as 74 per cent. of incombustible diatomaceous earth.

Workmen's clothing must be stored out of the way of coal dust, since if the clothing gets greasy in wear, and also covered with coal dust, it may become pyrophoric.

The suddenness and violently destructive effects are well illustrated by the following practical example, wherein an explosion was produced through a workman letting his hammer fall to the bottom of a large storage vessel containing a layer of lignite dust. The shock drove the dust upward in clouds, and the spark struck by the hammer against the metal immediately produced an explosion which destroyed the whole.

### 3. Coal Dust Fuel

The high temperature furnished by burning coal in the form of dust is due to the complete combustion of the carbon. Attempts have been made at the technical utilisation of this fact by the introduction of coal dust firing, which, however, despite the advantageous utilisation of the calorific value of the coal, has not yet succeeded in displacing the ordinary method of coal firing. Nevertheless, the development of the system is so promising that insurance companies will certainly have to reckon with it in the future.

In itself the system is simple, the coal being finely ground (unless already in a pulverulent condition), intimately mixed with air by means of an automatic blower, and conducted into the furnace, where it burns.

In this manner every particle of coal is enveloped by a sufficient quantity of oxygen (air) for its complete combustion, and is entirely consumed, without any appreciable formation of smoke. In order to still further increase the already very powerful heating effect, the current of air is heated by the escaping furnace gases. Even steam is

added to further heighten the temperature by means of the liberated hydrogen (explosive with air).

The system is not exempt from highly dangerous factors. The great heat of the flame ( $2000^{\circ}\text{C.}$ ) is sufficient to melt the boiler tubes, and also causes irregularities of temperature in the firebox; it is dangerous to start the firing in a cold boiler; the grinding of the coal into dust generates great heat, accompanied by the presence of coal dust in the enclosed apparatus, and finally there is a possibility of an explosion of mixed coal dust and air in the storage receptacle, wherein the mixture is formed and kept in constant motion. The danger is increased on the introduction of steam, by the formation of hydrogen.

In coal dust firing the combustion itself is of an explosive character.

Another circumstance may lead to additional dangers; since the coal cannot be ground to the requisite degree of fineness unless perfectly dry, an artificial drying of the material must be performed on the spot. This makes the entire plant very complicated, and a dangerous character is imparted by the interruptions, which are frequent. At present this system has not yet attained its culminating point; and even when ultimate perfection is attained very careful attention will always be necessary, owing to the ever-present risk of explosions, for directly anything goes wrong with the working a condition of danger is established.

The dangers of spontaneous explosion and the accumulation of explosive coal gases may be diminished, if not entirely obviated, by efficient ventilation, or rather, by superficial cooling. Since the main danger consists in an accumulation of heat in the interior of the heaps, the surface must be kept cooled down to such an extent that it will absorb any heat generated in the interior, and radiate same into the air.

It is, however, necessary that the commencement of ventilation should not be postponed until heat has already accumulated in the heap, but should start immediately the coal is placed in store, piled in moderately high heaps in a well ventilated chamber that is protected from the sun and all other sources of heat. This precaution is only essential where the coal is to be stored for some time, and is particularly bituminous and gassy, with a decided tendency to spontaneous ignition. Coals of unknown character should be handled with caution until their harmlessness has been demonstrated. In low stores with insufficient ventilation it is often the custom to make air flues in the heaps themselves, with the idea that this will afford sufficient protection against spontaneous heating. Experience on shipboard, however, has shown that wooden shutters for this purpose do not answer, their dimensions being insufficient to thoroughly ventilate the heaps, which are often of considerable size, this being more particularly the case when the lumps are small and the circulation of air is retarded locally by the pulverulent condition of the mass. When local overheating occurs in the vicinity of a ventilating flue the latter may constitute a positive source of danger, by supplying oxygen (air) to the heating coal and thus favouring ignition. These spots have been identified as the seat of outbreaks of fire, so now it is preferred to cut off all supplies of oxygen to the interior of the heaps, and to merely keep the surface temperature down well.

Trials have also been made with hermetically closed bunkers, but

without much result, the chambers becoming filled with gases from the coal, and therefore extremely liable to explosions.

The means for preventing spontaneous ignition in coal may be summarised as follows:—

Abolishing the sprinkling of pyritic coals.

Excluding from prolonged storage all damp and pyritic coals.

Limiting the height of the coal heaps to 10 feet.

The store must be protected from soil moisture, high, and capable of thorough ventilation. The coal must be protected from the sun or other source of heat, and must not be allowed to exceed a temperature of 80° F.

Pit-damp coal, especially when pyritic, must first be allowed to dry in the air before it is piled up for storage. The risk of bunker fires and explosions is diminished by exposing the coal to the air for three weeks before loading. The introduction of a lateral supply of air into the heaps must be avoided, and in fact should be prevented by the erection of a low protecting wall all round.

All pyrophoric substances or waste capable of exerting a similar action must be rigidly excluded.

When any considerable spontaneous heating is detected in the heaps, an attempt must be made to cool down the warm coal by removing the top portions and spreading out the rest.

Water is not to be used for cooling unless the heating has proceeded so far that the coal is beginning to burn; in that case the coal must be regularly drowned with water, but unless the available water supply is sufficient to enable this to be done, watering must be dispensed with altogether, as merely favouring the spread of fire. Quenched coal should be spread out until dry. When the storage chamber is so completely enclosed that it can be filled, and the air completely displaced by introduced steam or carbon dioxide, this plan is highly commendable; the steam or carbon dioxide, however, must be forced in from below and directly into the heaps.

#### 4. Briquettes

Briquettes are, *per se*, less dangerous than loose coal, though liable to spontaneous ignition, when, as is often the case, they are placed in store whilst still hot from the factory, and are piled in high, broad heaps.

Indeed, one can almost speak of a season for briquette fires (of which there were fifty-four in Berlin alone, in the years 1889–91), namely, in the hot weather, when the power of the sun is at its height. If several loads of briquettes be left out in the sun, and then stored hot, it often happens that the mass begins to heat, slowly, though appreciably, at first, and afterwards developing into spontaneous ignition.

So long as briquettes are still warm or are exposed to any source of heat during storage, they should not be piled more than 10 feet high and the same in breadth, a free space, for a proper circulation of air, being left between the rows.

Briquette-making is a very dangerous operation, though the risks have been considerably reduced by the improvements introduced, based on the experience of years.

The material is generally lignite, waste coal or slack, held together by some binding ingredient like coal tar, resin, pitch or asphaltum, an

pressed. At present high pressure is employed to generate heat, which softens certain constituents and binds the mass together. For briquettes of coal dust and asphaltum, the dust is first heated to 119° F. and the asphaltum to 338° F.

According to circumstances, the materials, which are often very damp from the pit, are first pulverised and dried by the aid of steam, hot air, or furnace gases, at a temperature of 158°–168° C. or 320° F. The crushing and sifting processes furnish a deal of dust, which may produce dust explosions (*q.v.*), especially in presence of hot air; and the danger of drying is augmented by the presence of a high percentage of sulphur or bitumen. Most of these explosions occur in the conveyors and elevators, between the oven and the press. The drying ovens are laden with dust, which should be prevented from accumulating whenever possible, and should not be stirred up any more than cannot be avoided. The prepared material is then subjected to a pressure of 1200 atmos. at a high temperature, the pressing itself contributing to the generation of heat. The briquettes are still hot on issuing from the press, and if stored in high heaps, or long exposed to the sun, while in this condition, are very liable to take fire spontaneously.

We have just seen that coal, *i.e.* a substance in which carbon in a loose state of chemical combination forms the main constituent and plays the principal part, may be a material of very dangerous character. There are, however, numerous other substances in which carbon also plays an important rôle, but in which its presence cannot be detected by their external appearance; such compounds include benzol, naphthalene, acetylene, methane, carbon disulphide, &c., and most of them are far more dangerous than coal itself. These will be dealt with separately later on; but we must now treat of the carbon compounds known as carbides, which are of considerable importance.

### 5. Carbides

Carbon combines with a large number of elements, and when these elements consist of metals or substances of metallic character, the compounds are termed "carbides."

This term does not include the compounds of carbon with hydrogen, the so-called hydrocarbons, benzol, toluol, acetylene, naphthalene, and methane.

With chlorine, carbon tetrachloride.

With nitrogen, the inflammable gas, cyanogen.

With sulphur, the dangerous carbon disulphide.

With boron, carbon boride.

With silicon, carbon silicide (carborundum).

With oxygen, carbon dioxide and the dangerous carbon monoxide.

Of itself, carborundum (also known as silicon carbide) is quite harmless; but its preparation, from sand, coke, sawdust, and common salt, in the electric furnace, is attended with numerous dangers. For instance, a large quantity of carbon monoxide is liberated, which rushes out all aflame and envelops the furnace in fire. If the gas be prevented from escaping through the crevices it bursts the furnace, and the burning gases and sodium vapour (from the salt) and glowing ashes cause an outbreak of fire.

On the other hand, the following compounds of carbon with metals are true carbides (formerly known as carburets). The table also displays their behaviour in presence of water, the resulting inflammable gases forming their principal danger.

Kind of Carbide.	No. of Gases furnished with Water.	Name of Gas.	Dangers of the Gases.
Potassium	one	Acetylene	When mixed with air and under a pressure of 2 atmos. and more, highly explosive.
Sodium	one	"	"
Lithium	one	"	"
Calcium	one	"	"
Barium	one	"	"
Strontium	one	"	"
Magnesium	one	"	"
Aluminium	one	Methane	Explosive with air.
Beryllium	one	"	"
Cerium	two	{ Acetylene and Methane together }	As above.
Lanthanum	two		
Yttrium	two		
Thorium	two		
Manganese	two	Acetylene and hydrogen	Hydrogen explosive with air.
Samarium	several	Acetylene and complex hydrocarbons	Explosive with air.
Uranium	four gases, together with liquid and solid hydrocarbons	Acetylene, methane, ethylene, and hydrogen	All dangerous and explosive.
Iron	two	Hydrogen and carbon monoxide	The liberation of gas begins at 140° C. This carbide is also pyrophoric.
Gold	none	...	Gold carbide, however, explodes under shock, percussion, or heating.

Except in the case of iron carbide, the liberation of gas begins at the ordinary temperature, and even in damp or foggy weather, so that the presence of liquid water is not essential for the production of the inflammable gases.

The degree of danger depends, not on the number of gases liberated, but on the ease with which they are disengaged, and the volume produced, which differs in the various carbides. Thus, 1 lb. of calcium carbide furnishes 4-4½ cubic feet of acetylene, whilst lithium carbide gives 8-9 cubic feet, or twice as much, which means a decided increase in the danger (or at any rate the power) of explosion.

In the case of two carbides furnishing an equal amount of gas, that one is the more dangerous which produces the more impure gas, or mixed gases. This is particularly so with acetylene (*q.v.*), the explosion risk of which increases with the percentage of other gases present. This forms the basis for judging the various carbides.

The only carbide with which we have to deal as a commercial article is calcium carbide. Now this carbide is not very productive in respect of gas, and in fact can only be successfully introduced as an illuminant

where there is no competition; as soon as the other carbides can be produced cheaply (which is only a question of time) they will be certain to displace the calcium compound. Whenever this result is accomplished, acetylene will become more prominent as a competitor of other illuminating agents.

The following remarks apply to all carbides that give off gas at the ordinary temperature when brought into contact with water: Carbides should be handled, packed, and stored like preserves; and just as these latter are damaged by any access of air or moisture, so is it with the carbides, a small amount of moisture causing liberation of explosive gas. For this reason, vessels containing carbides must be kept tightly closed.

Where bulk has been broken, and the contents of the package have already attracted moisture, arrangements must be provided for enabling the subsequently liberated gas to escape from the closed package, otherwise the latter will be in danger of bursting. A very small orifice will suffice for this purpose, but wherever possible the provision of a valve is advisable. Rooms where such carbide vessels are kept must be regarded as in imminent danger from explosive gases, and never visited with lights, or heated or illuminated by open fires. The same applies to filled vessels that have become defective. The soldering of such vessels is a highly objectionable practice, on account of the use of possibly uncovered soldering flames; and violent explosions are possible under these circumstances.

In any case, stores of carbide must be kept very dry, and only in fire-proof rooms, from which all open flames or fires are excluded.

Should a fire break out in a carbide store, the use of water as an extinguishing agent is open to grave objection, since very violent explosions may ensue as soon as the water comes in contact with the carbide.

Carbide storerooms must always be kept under lock and key; and legible notices must be posted up at the doors prohibiting unauthorised entry, smoking, and the introduction of open lights or fires. The ventilation arrangements must be such as to permit the escape of acetylene or other disengaged gases in all directions. Droppings of spent carbide invariably contain some *undecomposed* carbide, and must therefore be handled with care, not thrown into the fireplace, on compost heaps, down lavatory pans, into ashpits, &c.

Deep, dark cellars are unsuitable for storing carbide.

The danger of carbide is not confined to the liberation of gas, but extends also to the heat disengaged when it is brought into contact with water, especially when the amount of the latter is small. This behaviour resembles that of quicklime, which, in presence of about one-third of its own weight of water, enters into combination therewith and may become red-hot in the process. In the case of carbide, the heat thus generated may attain 800° C., a temperature sufficient to ignite the acetylene liberated (see *Acetylene, Dropping System*).

Attempts have been made to diminish the danger of calcium and other carbides by impregnating them with oily or greasy substances like petroleum. This treatment considerably retards, without, however, entirely preventing, the liberation of gas by water, damp air or fog, since it renders the carbide more difficult of access by moisture.

The not infrequent practice of mixing calcium carbide with hygro-

scopic substances (calcium chloride, zinc chloride, magnesium chloride, &c.), dried at  $120^{\circ}\text{C}$ ., is dangerous on account of the continuous absorption of moisture, it being possible, under these conditions, for a quiet liberation of acetylene to proceed unnoticed.

Carbide is less dangerous when the liberated acetylene is pure and free from phosphoretted hydrogen (see *Acetylene*).

Calcium carbide is prepared on a manufacturing scale—with which alone we have to do at present—in the electric furnace, at a temperature of about  $3000^{\circ}\text{C}$ ., by exposing quicklime and charcoal to the influence of the electric arc, whereupon the carbon and lime combine to form calcium carbide. This method is only applicable to the carbides of the alkaline earths (calcium, barium, and strontium) and the heavy metals. The carbides of the alkali metals (potassium, sodium, and lithium) are prepared from the metals and acetylene, a dangerous process owing to the ready inflammability of both components.

The electric furnace is a source of danger, not merely on account of the high temperatures developed, but also from the inflammable carbon monoxide produced abundantly in the preparation of carbide. Risk of explosion is therefore to some extent imminent, though capable of amelioration by the employment of suitable devices (doors and covers).

At present, carbide is chiefly used in the production of acetylene for lighting purposes; it may, however, be expected that this substance, which is of great importance to the chemical industries, will come into more general use. In fact, it is already said to have done good service in metallurgy for dissociating ores. When these are mixed with carbide, a considerable amount of heat is developed, and, in the case of copper- or lead chloride, the mixture can be lighted with a match. This inflammability of otherwise incombustible substances is due to the liberation of acetylene, which in this event is generated without water. Other by-products are formed in the reaction, *e.g.* benzol (at  $600^{\circ}$ – $800^{\circ}\text{C}$ .), naphthalene (at  $800^{\circ}$ – $1000^{\circ}\text{C}$ .), and anthracene at still higher temperatures. This last named product is perfectly innocuous.

When mixed with slaked lime and heated to  $400^{\circ}\text{C}$ ., calcium carbide liberates acetylene without the aid of water.

Of the other carbides, which are still little known bodies, it will be sufficient to state:

That iron carbide may, under certain conditions, be pyrophoric; it ignites direct at  $302^{\circ}\text{F}$ .;

Gold carbide produces a flaming explosion under slight shock or percussion, and is therefore capable of igniting;

Sodium carbide, a white powder, is raised to incandescence by chlorine gas, also in carbon dioxide and sulphur dioxide. It explodes in contact with water or with bromine vapour. Similar behaviour is exhibited by the carbides of potassium and lithium.

It follows, as a consequence of the somewhat dangerous character of the carbides, that all factories where these substances are employed should specify the kind in use; and that insurance companies, in accepting risks, should not rest content with mention of the term "carbide," which in current parlance is restricted to calcium carbide, one of the least dangerous members of the group.

## CHAPTER XXXIV

## FIBROUS MATERIALS

## 1. Fibres in General

THE materials here coming into consideration include wool, silk, cotton, hemp, flax, tow, jute, nettle fibre, mungo, shoddy, cotton waste, and artificial silk.

Differences exist in the fire risk and inflammability of these substances. The factors determining the former quality are physical condition, behaviour towards heat, fire, wet, electricity, fats, oils, and chemical reagents. The tendency to produce dust (of which cotton furnishes up to 14 per cent. in treatment) also increases the danger, by virtue of the possibility of dust explosions.

As regards physical constitution, cavities in the individual fibres of the material play an important part. All hollow fibres are more dangerous than solid ones or such as are filled with any substance, the air in the cavities furthering oxidation, combustion, and the spread of flame. Furthermore, among the hollow fibres, those with wide cavities are more dangerous than those wherein the cavities are narrow.

The animal fibres, wool and silk, which are in general less in danger from fire than the vegetable fibres, are devoid of cavities.

On the other hand, cotton, flax, jute, hemp, and nettle fibre contain cavities (lumen), cotton exhibiting the largest and nettle fibre the smallest. In jute the cavities are alternately wide and contracted. The higher the temperature a fibre will stand without any important alteration, or sustaining any loss other than water, the smaller its fire risk. This maximum temperature is, in the case of silk, 248° F.; wool, 230° F.; cotton, 221° F.; other vegetable fibres, 212°–221° F.

Here, again, the animal fibres exhibit greater resistance and diminished risk, though, on the other hand, they retain heat more tenaciously than vegetable fibres, this capacity being greatest in the case of silk, wool, cotton, jute, and hemp, in the order given. Thus, three equal sized balls, uniformly heated to 208·4° F., gave the following readings:—

	After 0 Minutes.	After 10 Minutes.	After 22 Minutes.	After 30 Minutes.	After 40 Minutes.	Total Decrease.	Decrease in 10 Minutes.
Silk . . .	208·4°	172·4°	100·4°	89·6°	78·8°	129·6°	36°
Wool. . .	208·4°	145·4°	84·2°	77·0°	69·8°	138·6°	63°
Cotton . .	208·4°	125·6°	73·4°	69·8°	64·4°	144·0°	82·8°

The superior retention of heat by silk is more clearly exhibited during the first 10 minutes, the percentage radiated in that time being only 20·4 per cent., and by wool only 35·7 per cent., whereas cotton lost 46·9 per cent. of its heat in the same time.

The behaviour of the various fibres in flame and fire is very different, the vegetable fibres burning readily and briskly, with the formation of only a small quantity of dullish charcoal; once lighted they are able to continue burning. On the other hand, the animal fibres burn sluggishly, are not so easily kindled, and can only be induced to continue burning when the combustion is supported by an extraneous flame or source of heat. They furnish a large proportion of spongy charcoal, which will not continue to glow or burn unless in a strong draught.

The cause of this difference is to be sought in the presence or absence of internal cavities in the fibres; these cavities also play a considerable part in the spontaneous ignition of fibres, and render the vegetable fibres more dangerous in this respect than those of animal origin.

Though agricultural products and other organic matters can be brought to a state of spontaneous ignition by the presence of wet and moisture, the fibres remain indifferent and cannot be so induced, even with an abundance of moisture. Only in cases where other factors co-operate, such as pressure, presence of fats, &c., which of themselves are sufficient to incite spontaneous ignition, is this tendency enhanced, pressure effecting this result in presence of a high proportion of moisture, and fat aiding when the moisture is too low.

Hence a large percentage of moisture is only dangerous when the fibres are simultaneously subjected to heavy pressure, the two factors in conjunction increasing the power of retaining heat. When fatty matter is present, the tendency to spontaneous ignition is augmented by a low percentage of moisture, especially when pressure is also applied! Even fibres that have been dried and oiled become very fiery when pressed; and wool containing less than 12 per cent. of moisture should not be oiled at all. In fact, moisture plays a very important part in this matter, the desirable and minimum percentages being as under:—

	Per Cent.	Per Cent.
Wool . . . .	18·2 desirable	12 minimum,
Silk . . . .	11·0 „	10 „
Cotton . . . .	8·5 „	7 „

otherwise the liability to take fire spontaneously is increased.

The percentage of moisture in the air of the rooms where these fibres are worked is also an important factor, since, if the air be too dry, the fibres are electrified by their mutual friction. In such event, provision must be made for humidifying the air, the following degrees of *relative* moisture being essential:—

In worsted spinning . . . .	at least	80 per cent.
„ cotton spinning . . . .	„	60–80 „
„ weaving with dry wefts . .	„	70–80 „
„ „ „ moist wefts . . . .	„	60–70 „

The hygienic norm for the air of rooms is 30–60 per cent. of relative moisture, and therefore it is evident that this limit must be considerably exceeded if the risk of fire from electrical causes is to be prevented (see later).

According to some observers, certain impurities in the fibres shelter

thermogenic and zymogenic bacteria, and play some part in the spontaneous heating of oiled fibres. Thus Cohn found, in waste fibre, numerous micrococci, which induce a thermogenic fermentation process, and only cease their pernicious activity under the influence of hot steam or hot air. In the opinion of others, however, bacterial agency is devoid of importance in connection with the inception and continuance of spontaneous heating, the latter resting solely on purely chemical reactions. This latter view, which is now general, was experimentally demonstrated to be correct by R. Kissling.

The dangers of oiled fibres will be discussed later on.

Immersion in nitric acid nitrates fibres and imparts to them the dangers exhibited by nitro-compounds (*q.v.*); hence the storage of fibrous materials in the vicinity of (strong) nitric acid should be prohibited.

The water-proofing of fibres and textiles does not diminish the inflammability and combustibility, unless the substances employed contain antipyrenes. Now, this is rarely the case, these substances, on the contrary, being often very dangerous, consisting as they do of fatty materials, wax, indiarubber, caoutchouc, and paraffin, which are soluble only in inflammable media like petroleum ether, benzol, ether and spirit. These solutions are laid on, or else used for immersing the fabrics, which are then hung up to dry, the vapours furnished by the solvents forming atmospheres that are often very explosive.

A peculiar phenomenon is exhibited by animal and vegetable fibres, even when devoid of fat, on being dipped in ether, then opened out, and, after the bulk of the ether is evaporated, gently warmed, or pressed on a hot plate. In a few seconds the fibres become surrounded with an aureole exhibiting a bluish luminosity in the dark, and accompanied by the liberation of malodorous vapours. If the application of warmth be continued, the fibres take fire; and should the latter be even slightly browned or charred, the ignition will occur at far lower temperatures.

This phenomenon may be explained on the ground of electrical excitation; a more feasible hypothesis, however, is that the finest fibres decompose ether vapour at a moderate temperature, or cause its ignition by means of the atmospheric oxygen condensed in their pores. The action of the fibres is therefore catalytic. The phenomenon is never observed in the case of mineral fibres (asbestos, spun glass, mica). The presence of fat is of no importance.

## 2. Wool

Animal fibre is less dangerous than vegetable fibre, but when the two are worked together they possess the character of the latter.

In its raw state, wool is rich in fat (grease), and the finer it is the more fat does it contain; the proportion ranges from 7 to 14 per cent. The danger resulting from the presence of natural or artificial fat in wool is only heightened when the material is put under heavy pressure or is very dry, in which event the accumulation of heat chars the internal portions of the mass.

The numerous impurities in wool are removed by the opener, which apparatus should be kept isolated and fireproof, on account of the danger of ignition. On the other hand, the process of scouring wool to remove

the grease is innocuous, the substances used being mostly of a harmless nature—weak lyes and soap; though if fat solvents (benzol, carbon disulphide, or ether) be used, the danger is admittedly high.

The very impure, crude wool fat (suint) is purified by means of the aforesaid dangerous solvents; and the operation, as well as the recovery of the purifying agents by distillation (very large quantities being in question), is attended with all possible dangers (vapour explosions).

The further treatment of the purified wool fat, in the preparation of soap stock, lanolin, and crude cholesterolin, by fractional distillation, is also dangerous by reason of the gaseous decomposition products formed. These products being inflammable and explosive, suitable means must be provided, in the shape of flues, &c., for conveying them to a safe place, remote from all fire and sparks.

The other impurities in wool are mostly of a vegetable nature: husks, seeds, burrs, straw, &c., and are eliminated by carbonising or carbonisation, an operation that must not be confounded with carburetting.

Carbonising means to char a substance or certain of its constituents.

Carburetting implies the enrichment of a substance (mostly a gas or vapour) with carbon, by the addition of hydrocarbons.

These vegetable impurities are charred at a far lower temperature than the animal fibre, in fact at about 212° F. To ensure uniformity in the reaction, the materials under treatment are impregnated with a harmless carbonising liquid, which may consist of:

Magnesium chloride . the carbonising temperature being usually 300° F.

Ammonium chloride . the carbonising temperature being usually 265° F.

Dilute sulphuric acid . the carbonising temperature being usually 175°–300° F., according to the strength of the acid.

Hydrochloric acid . the carbonising temperature being usually 250°–265° F., the so-called dry process.

After treatment with these agents, the material is dried at 250°–300° F. for 1–3 hours; a process not without danger.

The carbonised residue separated from the wool forms dangerous masses that contain pyrophoric carbon. They should be stored in a fire-proof place, and quickly destroyed, since they greedily absorb oxygen from the air, and are then liable to ignite spontaneously. To reduce this risk they should be thoroughly cooled down before exposure to the air, and should never be heaped up more than 20 inches high. Sometimes they are utilised, either by nitration or by further charring (for the manufacture of blasting explosives, and in the acetic acid, acetone, or colour industries).

The carbonisation of wool waste, in the manufacture of shoddy, is more dangerous than the corresponding process with raw wool, the mass of carbonised residue being greater and more inflammable.

Carbonisation is performed in stoves and drums at 175°, 195°, or 212° F. Considerable risk of fire is incurred, owing to the bulk of the material and the possibility of accidental contact with dropped matches, &c., and outbreaks of fire are by no means rare. The author has observed them to occur at 155°–165° F.; and at 230°–300° F. any kind of matches (phosphorus or Swedish) will kindle a fire in the mass.

Moving the wool about facilitates the striking of the matches, as does also the application of even slight pressure; whereas if the wool be left untouched for a week at the same temperatures, the matches will remain unlighted.

Apart from direct ignition, the most serious danger in the carbonising process is the formation of explosive vapours. The only remedy for this is to maintain a good circulation of air through the mass in the stove; frequently a very difficult thing to do.

Experiments performed with only small quantities of wool showed fluctuations of temperature to the extent of 63° F., owing to the great difficulty of uniformly distributing the mass of wool.

Where the air cannot circulate, the explosive vapours cannot be diffused; they therefore accumulate in the warmest places, and when the stove is emptied they form with the air explosive mixtures, which will readily ignite at a faintly glowing fragment of carbon. This gives rise to explosions of great violence, which are of most frequent occurrence when wool waste is carbonised.

In addition to good internal ventilation, the best remedies for this danger are: a careful supervision of the stove temperature, and the establishment of communication between the stove and a boiler, whence steam can be introduced into the wool immediately any sign of fire is detected.

When hydrochloric acid is used its gas is often passed through a superheater on the way to the stove, thus augmenting the general risk.

The wood with which the carbonising stoves are often lined is also damaged to no small extent by the heat of the process, especially when of a resinous character or very old (see *Wood, Steam Pipes*). Such wood should always be made flameproof by impregnation.

Apart from its combustibility, wool *per se*, as an article of commerce or raw material, presents few dangers. If it is oiled for certain purposes, the nature of the oil used determines the risk of or immunity from spontaneous ignition. It should, however, never be oiled unless the percentage of moisture is at least 12 per cent.; the natural humidity is 18 per cent.

The most dangerous oil is vegetable oil, the safest, mineral oil, though the latter may be objectionable when it contains paraffin. Oleonaphtha is said to be quite safe, and wool oiled therewith can be stored for a considerable time without risk.

This oil (or mineral oil) is often used in admixture with vegetable oils, *e.g.* Maury's Oleate. These mixtures are far less dangerous than vegetable oils alone, but they cannot entirely obviate the risk of spontaneous ignition (see *Impregnation of Fibres with Oil*).

The scouring of oiled wool, like that of wool in the grease, is quite safe when solutions of soap, lye, or alkali hydrosulphides are used. The operation is conducted at about 120° F. When alkali hydrosulphides are used, the liberation of inflammable sulphuretted hydrogen is inevitable, and care must therefore be taken to ensure the safe removal of the gas, by burning, &c.

If quicklime be also used, it must be handled with the needful precaution (see *Calcium*).

Wool is also loaded with starch, starch sugar or dextrin, up to 10 per cent. of its own weight. Though this treatment does not increase

the danger in the same degree as with silk, loaded wool, being mixed with substances that are more combustible than itself, always burns more readily than when in an unloaded condition. The extent of the danger depends on the nature of the loading material; if the latter be dusty it renders the wool more liable to take fire.

The aptitude of wool for taking fire, spontaneously or otherwise, may be considerably facilitated by the presence of dyestuffs, some of which are capable of igniting spontaneously. Special risk attaches to wool that has been badly dyed, re-dyed, or met with any accident in the dyeing process.

Wool bleaching is a safe operation, the agents—of which hydrogen peroxide is the most explosive—being used in such a dilute condition as to be devoid of danger.

For the behaviour of wool towards electricity, see *Dry Cleaning*.

### 3. Silk

In general, silk is the least dangerous of all fibres, and will stand warming up to 250° F., or even 390° F., without undergoing alteration. Being solid, it burns with difficulty, but, on the other hand, tenaciously retains the heat once absorbed, more so indeed than any other fibre. It has a powerful attraction for moisture and other (even solid) substances, and readily fixes them; hence the ease with which it can be loaded with substances, often of a dangerous character.

The natural humidity of silk is 10–15 per cent., but it can readily absorb and retain up to 30 per cent. of moisture. To expel this moisture a temperature of 248° F. is required, the highest drying temperature of any fibrous material.

Of itself, silk is not liable to spontaneous ignition, though it may be made to acquire this faculty by dyeing (loading), tannin, oils and chemical salts. It is these substances, of which silk may absorb up to 300 (or even 500) per cent. that cause the spontaneous ignition of silk goods, formerly a somewhat frequent occurrence. The same effect may be produced by oiling, though the tendency thereto is less in this than in other fibres.

Loading is an essential operation for certain classes of silk goods, in order to increase the closeness of texture and improve the feel. Thus, tassels and fringes would not “hang” properly unless loaded.

Loading with up to 60 per cent. of foreign substances is classed as “light”; up to 150 per cent. as “medium,” and up to 300 per cent., “heavy.”

Silk when loaded behaves, not like the horny substance wool, but like a tanned skin, swelling up and presenting a larger surface; the porosity is increased, so that loaded silk can absorb still more moisture than usual.

The principal loading and dyeing materials for silk comprise all substances containing tannin—*e.g.* chestnut extract, catechu, logwood extract, gall nuts, tannin, in combination with iron salts, both ferric and ferrous.

The following are also used: wood vinegar, tin salts, antimony compounds, picrates (especially the dangerous lead picrate), gum, fats, and Berlin blue.

It is to the researches of Prof. E. König, of Crefeld, that we are

indebted for the unveiling of the mystery attaching to the spontaneous ignition of silk. The causes of this phenomenon are as follow :—

The loading materials are deposited irregularly on the silk fibres, and hence a portion of them gets rubbed off, accumulates in some part of the mass, and there constitutes a centre of ignition; whether an outbreak occurs or not depends on the composition of the loading materials themselves.

If the loading contains ferrous compounds (poor in oxygen) and tannic acid, the material forms a powder that will smoulder in contact with warm wire. Silk loaded in this manner will take fire of itself on being warmed to 230° F. and then exposed to the air. Even these slight incentives are not always necessary. As already mentioned, loaded silk swells up considerably, becomes more porous, absorbing moisture, and at the same time oxygen, with avidity. The ferrous compounds present have a strong tendency to oxidise into the ferric condition; they combine with the absorbed oxygen, and sufficient heat is generated by the reaction to ignite the readily inflammable loading agents—*i.e.* the oxidation is accompanied by pyrogenetic phenomena, the silk becomes incandescent and takes fire. Great assistance in this reaction is afforded by the capacity of the silk for accumulating and retaining heat.

When ferric compounds are used for loading silk, the oxidation and generation of heat do not occur, and no ignition takes place, unless tannin be employed as the source of the tannic acid in loading. Even in this event, however, ignition is more difficult to accomplish, the silk requiring to be heated up to 284° F. before it will take fire on exposure to air.

Should the weft alone in silk fabrics be loaded, and not the warp as well, only the former will smoulder.

Lead picrate imparts a certain tendency towards spontaneous ignition (see *Picrates*) in silk fabrics; on the other hand, the stannic compounds are innocuous.

The results of the observations made in this connection show that the early stage of spontaneous ignition, viz. charring, mostly appears in the centre of the bale, smouldering and actual ignition only commencing when the bale is opened and air gains access, or when the internal charring has opened up a way to the outside air. A bale may be charred inside without any outward indication being afforded of its condition.

For insurance companies it is a matter of importance to ascertain the nature and composition of the loading materials used, more particularly when they consist of ferrous compounds or tannin, and also to what extent (percentage) the loading has been pushed.

Little or no danger attends the treatment of raw silk in its pure state, such as scouring, gumming, bleaching, sulphuring, &c., all these operations being conducted at temperatures far below the boiling point of water, and with innocuous materials, *e.g.* soap, soda, and cream of tartar. Occasionally, it is true, use is made of sulphur dioxide, eventually in steel cylinders under high pressure. With regard to the gassing of silk, see *Cotton*.

#### 4. Artificial Silk

In order to comply with the widespread desire of the public to wear silk, it will readily be understood that attempts have been made to dis-

cover a cheap substitute for the more expensive natural article. These endeavours have led to the establishment of an extensive industry, which, however, insurance companies have no cause to welcome with any special pleasure, since it is to a large extent attended by no little danger.

Before the stage of producing artificial silk, as we now know it, had been reached, endeavours were made to produce a silk substitute from spun glass, and also by suitably treating other natural fibres. Thus a lustre was imparted to cotton by treating it with wax and starch, or by mercerisation (so-called after John Mercer, the inventor of the process). This last operation consists in treating cotton, under tension, with caustic soda, and then drying it, still in the same condition. These processes are free from danger, and the same remark also applies to the manufacture of gelatin silk.

The dangers began with the introduction of cellulose silk, and increased considerably in the case of collodion and nitrocellulose silk.

Cellulose silk (chief processes that of Langhans and Dreaper-Tompkins) is prepared from cellulose, and as this is not nitrated, the risks of that operation are avoided, though the process is rendered dangerous by the use of spirit, methyl alcohol (wood spirit), acetone, and compound ethers of very low boiling point and high inflammability. These and similar liquids are employed to precipitate the silk stock, prepared from cellulose and sulphuric acid, the quantities used being so great as to make the recovery of the spent liquids profitable. This operation, of course, presents dangers of no small magnitude.

On the other hand, the product is not more dangerous than natural silk as an article of commerce or storage; and, in fact, is much safer in respect of spontaneous heating and the retention of warmth.

With regard to this class of silk, of course, a guarantee must be demanded that it has been prepared from cellulose alone, not from nitrocellulose; for as soon as this latter kind of artificial silk comes into question, there arise the dangers inherent in nitro-compounds (*q.v.*).

Factories in which artificial silk is made by the Chardonnet, Cardaret, Vivier or Lehner processes employ explosive nitrocellulose, often in very large amount, some works using 8, 10, 12, or 18 cwt. daily in a single operation, along with enormous quantities of ether and alcohol.

As it is not every commercial grade of nitrocellulose that is suitable for making into artificial silk, the factories prepare their own, in somewhat the following manner:—

Drying the cellulose at 285°–320° F.

Converting it into nitrocellulose or pyroxylin (*q.v.*).

Neutralising the acidity, and draining the nitrocellulose in hydro-extractors.

Dissolving this product in alcohol-ether, acetone, toluol, wood spirit, and camphor.

Filtering and pressing the solution through extremely fine capillary nozzles under high pressure (15–40 atmos.).

The extremely fine threads of nitrocellulose issuing from these nozzles part with the solvent, by evaporation, on exposure to the air, and become solid. Occasionally they are dried over a steam cylinder. In either case the vaporised solvent forms explosive mixtures with air and render the operation highly dangerous in view of the large quantities involved.

In other methods the nitrocellulose solution is forced through similar nozzles into a solution which causes it to solidify, the nitrocellulose being insoluble in the liquid employed. This latter consists of turpentine, chloroform, juniper oil, or of carbon disulphide, benzol, and petroleum, *i.e.* dangerous liquids. In some establishments the composition of the liquid is maintained secret.

Since artificial silk composed exclusively of cellulose would be too dangerous for general use, it has been de-nitrated by means of sulphur solutions, alkali sulphides, calcium sulphide, or ammonium sulphide. This treatment has been claimed to obviate all the dangers of artificial silk; but this is not altogether the case, it being impossible to push the operation so far as to eliminate the whole of the nitrocellulose, since that would spoil the appearance, &c., of the silk; and, moreover, complete denitration is not so easily effected in the case of such large quantities.

For this reason, artificial silk still retains some risk of inflammability. Experiments conducted with such artificial silk by the author gave the following results: certain isolated fibres exhibited particular susceptibility towards flame; when exposed to a small gas flame, at a distance of 6 inches, the silk charred in two hours, the temperature at the seat of carbonisation measuring  $135^{\circ}\text{C}$ .; on reducing the distance to 4 inches, the temperature rising to  $230^{\circ}\text{C}$ ., the threads took fire and burned immediately when in a loose state, detonating quickly; more slowly, though still violently, when in a compressed state; and when tightly compressed more slowly still, the individual projecting threads, however, quickly igniting and conveying the flame to the entire mass, where it spread.

It is thus evident that, wherever any possibility of ignition is present, good packing is essential for artificial silk. In work, care should also be taken to remove any small pieces of waste, these being highly calculated to transmit flame.

Should a cloud of dust arise from artificial silk, more particularly in presence of a naked flame, extremely violent dust explosions may be expected.

On account, therefore, of the fiery and explosive character of the materials, the employment and recovery of large volumes of inflammable liquids, and the ready inflammability of the finished product, the manufacture of artificial silk must be classed as a process of special danger.

A safer process is that of Langhans (and to some extent also that of Lehnert), wherein pure cellulose alone, with little or no nitrated cellulose, comes into employment. In insuring such factories, the exclusion of nitrocellulose from the process must be definitely proved.

*Table of the Chief Processes for Artificial Silk.*

Process.	Materials used.	Composition of Solidifying Liquid.
Langhans . .	Cellulose and sulphuric acid	Spirit, wood spirit, acetone, ethers.
Chardonnet .	Cellulose + nitric acid = nitrocellulose Ether and alcohol, partial denitration	
Cardaret . .	Cellulose + nitric acid = nitrocellulose Ether, acetone, alcohol, camphor, castor oil	Water, and secret preparations.

## 5. Cotton

The fire risk of cotton is higher than that of any other fibre, on account of its hollow structure and the stimulative effect of the contained air on combustion. Phenomena indicative of combustion, at first manifested by merely a slight browning, commence at 221° F.; after a short heating at 230° F. considerable alteration is observed, at 320° F. considerable browning occurs, and charring at 446° F.

Even such minute sparks as are produced by striking the iron hoops on the bales are sufficient to cause cotton to smoulder, which condition is transmitted, through the fostering influence of the air in the fibres, to the interior of the mass, where it may continue unnoticed for weeks, the smell of burning being absorbed by the outer cotton or the carbon formed (*q.v.*).

Wet or moisture will not produce spontaneous ignition in cotton, though fat and oil will do so. In this case the course of events is that described in connection with fibres impregnated with oil; see behaviour in presence of moisture and electricity, mentioned at the beginning of the present section.

The greatest risk of spontaneous ignition is produced by vegetable oils, less by the animal fats, and least of all by mineral oil. In point of retention of heat, cotton is less dangerous than any other fibre. This has been already discussed.

The dangers of the cleaning and working of cotton are on a par with those of wool. In the processes of opening and scutching, cotton furnishes a larger percentage of dust (14 per cent.) than the greasy substance, wool; and this dust is readily exploded by contact with a small flame, in presence of an inflammable gas or vapour. For this reason, great care has to be exercised in securing the removal of this dust, by means of exhausts, acting direct on the cleaning machines so as to prevent dissemination of the dust in the air of the workroom.

The removal of oil (scouring) from cotton goods, yarns, &c., can be effected by perfectly innocuous detergents (magnesium chloride, alkalis), the dangerous solvents, ether, carbon disulphide, &c., being unnecessary. In the course of its further treatment, cotton has to go through two processes which must now be mentioned.

Gassing consists in passing the yarn, &c., through a small gas flame or over a red-hot metal plate, for removing the fine hairs and down, and imparting a smoother appearance to the goods. Under certain circumstances this operation, which is also applied to silk and other fibres, may be the cause of no small danger. Where it is carried on on a large scale (twist works), it produces a sooty dust that contains carbon monoxide; and should an accumulation of this dust occur in closed rooms, explosions on contact with open flame are not impossible.

Often times, when no coal-gas is available, the gas for this operation is prepared on the premises, from gasoline, petroleum ether, ligroin, &c. The apparatus is not free from danger (see *Air-Gas*).

**Animalising Vegetable Fibres.**—Unlike certain other fibres, cotton is not suitable for dyeing with certain dyestuffs. On this account it is animalised, or converted into amidocellulose, by heating it to 212° F. for about 6 hours in a solution of calcium chloride saturated with ammonia.

Sodium stannate, milk, albumin, casein, and alum are also used for the same purpose. The operation is quite safe.

Cotton furnishes nitrocellulose for blasting explosives and many other preparations (see *Nitration*).

Other dangers are incurred in connection with the further treatment of cotton. In the spinning sheds it is considerably endangered by the high speed of the spindles (up to 10,000 revolutions per minute), the heat generated by the rotation being increased by the use of bad lubricants; the greasy character of the machinery, utensils, flooring, waste; the storage of dried and dyed material in a warm condition or piled up; the influence of electricity on excessively dry cotton; all these circumstances make spinning works highly dangerous establishments.

With regard to oiled cotton, see *Impregnation of Fibres with Oil*.

### 6. Flax (Linen), Hemp, Jute

As is the case with cotton, these three fibres when oiled are exposed to the danger of spontaneous ignition, and under certain circumstances to a greater extent than cotton.

The preliminary treatment of flax and hemp is mostly carried on in water; and, when piled in heaps or compressed, the wet masses exhibit an objectionable tendency to heat spontaneously, and in some cases to ignite.

The danger of piling in heaps is greater in the case of jute, which is sprinkled with oil (soap and olein) in addition to water (in the batching process). The presence of the oil considerably heightens the temperature, which indeed may even attain the point of spontaneous ignition.

An important point with these three fibres is to keep all fatty substances at a distance, since even small quantities may lead to spontaneous ignition; and, moreover, the storage temperature should not be over warm. When in a pure and thoroughly dry condition, these three fibres may attain such a degree of desiccation, under the influence of moderate warmth, the radiant heat from a stove or piping, and in summer from the rays of the sun or being stored close under a roof, that pyrophoric carbon is formed and the mass takes fire. In this respect they are more susceptible than wood.

The residues left when these fibres are put through the cleaning process are known under the general name of "tow," a ligneous product that finds numerous applications. Tow is dangerous, inasmuch as it will glimmer at even 257° F., and is therefore one of the most easily kindled of fibres. When oiled, it has a greater tendency to take fire spontaneously than the purified fibres, and is specially dangerous, as regards retaining heat, if piled up in somewhat larger heaps than usual. For instance, in one case it was only discovered about half-an-hour before an outbreak of fire that a large pile of tow had become completely carbonised inside without exhibiting the slightest indication externally.

On the whole, it may be said of all fibres that the waste products are far more dangerous than either the crude or purified fibres themselves, and therefore they need more careful looking after. The chief reason for this dangerous character is the presence of dusty constituents, which greatly facilitate the reactions resulting in combustion. It is these dust constituents that also form the source of danger in other fibrous materials,

like old rope, fishing nets, string, &c.; and this risk is imminent in junk stores and other places where such goods are sorted, packed, and got ready for shipment.

These materials also give off certain gases during storage, which gases when mixed with dust and ignited by contact with a flame produce violent explosions (tow explosions), similar in character to those furnished by dust.

### 7. The Impregnation of Fibres with Oil

Under this heading we will consider the case of all fibres, and the waste, bye-products, and dust furnished by same, which have become more or less saturated by contact with oily, greasy, waxy, and paraffin-like substances.

Whereas neither the oils, fats, paraffins, or waxes on the one hand, nor the pure fibres on the other, are liable to take fire direct of their own accord, they incur this risk as soon as they are brought into intimate mutual contact.

It is difficult to properly apportion the blame for this peculiarity, since neither the liquid oils nor solid fats have any tendency to spontaneous ignition; and the same may also be said of the fibres, unless special circumstances intervene. Consequently the blame must be divided between them; the fibres taking a share because they absorb the oil into their minute pores, disseminate it over a large surface, and thus expose it to the action of large volumes of air or oxygen, whereby it becomes oxidised and laden with this gas; the fats and oils, on the other hand, in oxidising generate such an amount of heat that the readily inflammable fibres, provided they are able to absorb and retain this heat, first char and then take fire. Strictly speaking, however, oxygen should bear the entire blame of causing spontaneous ignition in this case.

These remarks apply, not merely to fibres, but also to all porous organic substances when impregnated with oil; *e.g.* sponges, sawdust, tapestry canvas, artificial flowers, yarns, carpets, paper, powdered and disintegrated waste, &c. Reference should also be made here to the dangerous operation of Turkey red dyeing, wherein the oil-soaked fibres and fabrics are piled in heaps for the purpose of fostering spontaneous heating to a considerable degree, not infrequently terminating in spontaneous charring and ignition.

The Turkey red process itself consists in treating vegetable fibres with alizarine, alumina, lime, and oil (usually castor oil), which latter has first been converted, by the action of sulphuric acid, into sulphuricinic acid, this being then combined with soda or ammonia to form the corresponding ricinate.

In this case, again, the oil-soaked waste material is far more dangerous than the raw materials and valuable products in the same condition; the relatively small amounts of spinning waste that are thrown away, moved by the wind, or dragged about by human or animal agency, are far more liable to spontaneous ignition than the large masses of oiled fibrous material that are being treated, always kept under the control of the operator, and never left quiescent long enough to take fire of their own accord, until the operations are completed.

The accidental dragging about of waste, &c. (which does not easily

occur with the goods in course of manufacture), is a not infrequent cause of fires, the origin of which long remained problematical. Similar fires have been induced in fibrous materials, fabrics, carbonised substances, metallic powders and metallic sulphides, by carriage and storage in vehicles or vessels that have become greasy from previous parcels of fatty substances. The regulations concerning the use and storage of oil-soaked materials and waste (even of the most worthless character) cannot be too stringent, or their observance too compulsory.

The reaction proceeding within the pores of the substance impregnated with oil is one of auto-oxidation. As already remarked, it is based :

On the one hand, on the mechanical attraction of atmospheric oxygen by porous substances, as in the case of charcoal ;

On the other, by the influence of this condensed oxygen on certain constituents of the fat, with which it combines ; and

Finally, on the resulting heat, the amount of which depends on the fineness of the pores, or the consequent dissemination of the fatty substance, and the large surface presented by the latter within a small space.

When a lump of fat or spoonful of oil, exposed to the air, turns rancid, the reaction is analogous to spontaneous ignition, except that owing to the comparatively small surface exposed the heat generated is quite insignificant and escapes observation, the surface being constantly cooled down by the air so that no accumulation of heat is possible.

In each of the innumerable pores of the oil-soaked fibre this reaction takes place, and in every individual instance warmth is generated which cannot escape. Moreover, unlike the lump of fat or spoonful of oil, these reactions, instead of proceeding gradually, are concurrent, so that a large amount of heat is produced at one time.

The coincidence of these innumerable reactions and heat-generating processes within a very confined space and short interval of time necessarily results in an enhancement of the temperature of the oil, fat, fibre, and oxygen. This increased temperature naturally accelerates the progress of the reactions, which in turn produces a further rise in temperature ; and thus the chemical processes and the generation of heat proceed hand in hand, their object being attained when spontaneous ignition occurs.

The accession of temperature produced at given intervals in the case of 50 grams of cotton, impregnated with 100 grams of linseed oil, was ascertained by R. Kissling, with the following results :—

Temp. :	23·5°	23·8°	23·8°	24·5°	25°	25·5°	26°	26·5°	28°	30°	32°	45°	94°	125°	170° C.
After hours:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15

at the end of which time spontaneous ignition supervened.

Almost all fats and oils are subject to auto-oxidation, though in some of them the degree is so slight that they may be used to impregnate porous bodies without spontaneous heating being produced ; this applies more particularly to pure mineral oils.

The degree of auto-oxidation also depends on the nature of the fibre, which, to some extent at least, has an important influence on the time

factor. According to circumstances, auto-oxidation may be either a very rapid or a very slow process; it can never be judged from any single standpoint, and therefore the question so frequently put forward for solution in cases of litigation, "When and within what period did the spontaneous ignition occur?" is one that can rarely be answered, and then only after a thorough investigation of the four fundamental details.

Auto-oxidation is greatly fostered by vegetable and animal fibres; but only very slowly by mineral fibres (asbestos, spun glass, and mica); and with these latter the process is never attended with high temperatures.

The presence of 5 per cent. of fat or oil may cause fibrous material to ignite spontaneously; and the amount may be increased to 200 per cent. without it being possible to say that the danger is thereby augmented.

In addition to the nature of the fibre and the percentage of fat, the following points have to be borne in mind: the duration and method of storage; the presence of other gases, vapours or carriers of oxygen; and the collaboration of a source of extraneous heat or sunlight, which strongly favours the process of spontaneous ignition, especially in the case of greasy rags.

On the basis of the very accurate researches of R. Kissling, the following general axioms may be employed in deciding on the cause of cases of spontaneous ignition.

The amount of heat generated in auto-oxidation depends on:

1. The area of the superficial contact between the fat (oil) and the air, *i.e.* on the porosity of the fibres;
2. The affinity of the oil for oxygen;
3. The degree of external cooling to which the object (fibre *plus* fat) is subjected;
4. The amount of extraneous heat supplied;
5. The sunlight.

The author would add to these the following factors, as being important in connection with the generation of heat:

The power of the pores for attracting oxygen,

The pressure set up in the substance by its own weight or in packing,

The degree of rancidity of the fat or oil.

According to Kissling, the activity of micro-organisms is here quite out of the question. They play a part in ungreased agricultural products, but not in this case.

Of all kinds of fats and oils the mineral oils (petroleum, solar oil, Vulcan oil, oleonaphtha) have the least affinity for oxygen (almost nil), and can therefore be used without objection for oiling fibrous materials. This safety, however, is dependent on the maintenance of normal conditions; and should these be removed, danger of spontaneous ignition is also incurred with the use of mineral oils, *e.g.* under the following circumstances:

When the mineral oil is impure, consisting of a heavy oil containing paraffin, and the impregnated material is hung on steam pipes, boilers, stoves, or in contact with some other warm object, or exposed to heat for some time; when the oil is strongly contaminated with sulphur or iron sulphide, from distillation products of lignite or coal, the presence of sulphur readily leading to the formation of iron sulphide which particularly favours spontaneous ignition in the oil and also in the waste

material. When the machinery is lubricated with mineral oil, some of the latter is bound to come into contact with the oiled fibrous material under treatment, and impart thereto the same tendency to ignition as is possessed by the cleaning waste.

The danger of spontaneous ignition in oiled fibrous materials may be diminished by an addition of 25-50 per cent. of mineral oil to the vegetable oil used, provided the mineral oil be free from paraffin and that the above mentioned abnormal conditions do not supervene.

According to Vuaflart, the following increase of temperature was obtained by oiling cotton waste with the mixtures specified below, the time required being also indicated in each case:—

Temperature:	428°	446°	226½°	213¾°	213¾° F.
in	4	6	6	6	7 hours.
Mixture:	Lard oil, Neat's-foot	Neat's-foot,	Neat's-foot,	Neat's-foot,	Neat's-foot
	alone	oil, alone	¼ Mineral oil	⅓ Mineral oil	½ Mineral oil.

The addition of mineral oil to the neat's-foot oil prevented the temperature rising much above 212° F., whereas in the case of pure animal oil it reached 428°-446° F. This is a very important feature, especially for oil rags, cleaning waste, &c.

Attempts have been made to render the troublesome greasy waste matter innocuous by pressing out the oil, but this is impracticable, some 8-10 per cent. of the oil being always retained, whereas 5 per cent. (and even under certain circumstances as little as 3 per cent.) being sufficient to cause spontaneous ignition.

Owing to the very divergent character of the fibrous materials it is almost impossible to establish a classification of the fats in the order of their power of imparting a tendency to spontaneous ignition in the former. It may, however, be taken for granted that the danger of the fats in this connection is in direct ratio to their iodine absorption value (amount of iodine absorbed by 100 grams of fat), and on this basis the following table has been compiled, the most dangerous fat being placed first:—

Vegetable Fat.	Iodine Value	Animal Fat.	Iodine Value
Linseed oil . . . . .	170	Codliver oil . . . . .	140
Hemp oil . . . . .	150	Seal oil . . . . .	127
Nut oil . . . . .	146	Japan liver oil . . . . .	120
Poppy oil . . . . .	138	Goose fat . . . . .	71
Olein . . . . .	138	Bone fat . . . . .	68
Cottonseed oil . . . . .	108	Hog fat, American . . . . .	62
Sesame oil . . . . .	106	„ German . . . . .	58
Rape oil . . . . .	101	Tallow . . . . .	42
Ground-nut oil . . . . .	96	Mutton tallow . . . . .	42
Castor oil . . . . .	84	Wool fat . . . . .	36
Olive oil . . . . .	82	Butter fat . . . . .	30
Palm oil . . . . .	52		
Cocoa butter . . . . .	36		
Palm kernel oil . . . . .	14		
Cocconut oil . . . . .	9		

Linseed oil is therefore the most dangerous, and is only surpassed in this respect by the same oil when boiled into varnish (see *Linseed Varnish*). Of the animal oils, the train (fish) oils head the list, but are not so dangerous as linseed and hemp oil. Rancid animal fats and oils (see later), however, are more dangerous than pure vegetable oils. Comparative experiments on the time needed for cotton waste to take fire spontaneously, when steeped in different fats, gave the following results, the mass igniting, with :

Linseed oil . . . .	after	1½	hours (temperature 167° F.) ?
Rape oil . . . .	"	10	"
Olive oil . . . .	"	6	" (temperature 149° F.) ?
Castor oil . . . .	"	24	"
Seal oil . . . .	"	2	"
Walrus oil . . . .	"	4	"

The fire risk of the chief fibres in an unoled condition is reversed by oiling, the danger then being in accordance with the extent of surface exposure afforded by the fibres, *i.e.* the finest and longest fibres are the most dangerous, the serial order being as follows :—

Silk, wool (animal fibres generally), then cotton, jute, and hemp. Considerable alteration in either case ensues when the supplementary influence of sunlight or any other source of heat comes into play.

The sun and heat must be carefully excluded wherever oiled fibres are in question, and suitable provision must be made to ensure cooling. Where, however, the application of warmth is inevitable, as in Turkey red dyeing (the oiled goods being piled in heaps in order that they may heat spontaneously), then the sole means of preventing this heating from proceeding to excess is by accurately checking the temperature in the goods by the aid of a thermometer, testing with the hand being insufficiently reliable.

Kissling found that fibres soaked with linseed oil, and exposed to direct sunlight, became heated to 266° F. in 4 hours, and afterwards took fire ; whereas in a check experiment, sheltered from the sun's rays, the temperature did not exceed 78° F. in the same time.

Spontaneous ignition is also favoured by a partial slight carbonisation of the fibre, or the presence of carbonaceous substances, such as the waste resulting from the carbonising process. Such substances have an increased absorptive power for oxygen, condense more of that gas in their pores, and thus enable it to exert a more powerful influence on the fat, and generate more heat.

The rancidity of the fats and oils facilitates spontaneous ignition in the fibres oiled therewith. If the oil or fat be already turning rancid, then the atmospheric oxygen has an easier task, and is able to combine more readily with the constituents of the fatty matter and hasten decomposition. Rancid animal fats will more readily induce spontaneous decomposition than good vegetable oils.

The application of pressure to oiled fibres has an indirect influence on their tendency to ignite of their own accord. The more tightly any substance is packed and compressed, the better is it enabled to retain warmth. Pressing reduces the influence of surface cooling, and the

internal heat, being prevented from escaping, remains within the mass of the fibrous material and there accumulates.

The large quantity of fatty substances used in the oiling of all kinds of fibrous material, justifies their recovery. No objection attaches to the washing of the fibrous material with soda, potash, lyes, &c., but often-times the material is piled in heaps to become warm, and is then pressed to extract the fatty substances, an operation that should only be performed under the observance of great precautions and in fireproof premises. Still more dangerous is the employment of solvents like benzol, ether, and carbon disulphide.

On the other hand, steam, which is one of the best means available for the purpose, is unobjectionable, provided the steaming is so complete that no trace of fatty matter is left behind in the fibres; otherwise great danger of spontaneous ignition will arise in the latter when subsequently dried by steam before use.

Establishments that undertake the task of removing fatty matters from oiled fibrous materials are very risky objects of insurance. They deal not only with fibres like wool and cotton, but also with filtering material (wood wool, sawdust, prepared paper) that has been used for filtering waste oil and fat; and such materials are also liable to take fire spontaneously.

There are no direct means of preventing spontaneous ignition in oiled fibres, even impregnation with antipyrenes failing to afford complete protection, especially in the case of cleaning waste. This treatment renders the fibres unflammable, but not the fatty matter, since this latter cannot be impregnated; hence charring is sure to occur, even though fire be prevented.

The best preventive of the danger involved consists in the employment of good oil, free from rancidity: pure vegetable oil mixed with 20-30 per cent. of pure mineral oil. Coal-tar oils cannot be recommended, owing to their irregular composition (presence of sulphur!); and animal oils are better avoided.

The workrooms should be cleared of waste oiled fibrous material and the like every day, the collected waste being then burnt.

Any cleaning waste or other greasy fibrous material in use should be kept away from all sources of heat, protected from the rays of the sun, and perhaps stored in a fireproof place during the night, preferably out of doors. All operations with oiled materials should be under thorough supervision, and the temperatures carefully checked.

The height of the storage heaps of such materials must be such as to prevent the lower portions being exposed to excessive pressure. Sulphur and iron sulphide must be kept at a distance from materials of this kind.

Attempts have been made to replace cleaning waste by paper, under the assumption that this (probably impregnated) paper is not liable to spontaneous ignition. This may be correct, but whether the spontaneous heating and ignition of the fatty substances can thereby be prevented seems very doubtful (see above).

Testing the liability of any fat or oil to ignite spontaneously is an easy matter: 7 grams of cotton wool are impregnated with 14 grams of the oil, &c., then lapped round the bulb of a thermometer, and the whole placed in a wire gauze cylinder (iron), which is exposed to a temperature

of exactly 212° F. in a drying oven. If, under these circumstances, the oven temperature remaining constant, the thermometer rises to about 392° F. within 2 hours, the oil must be discarded as one readily liable to spontaneous ignition.

Where an outbreak of fire has occurred in fibrous materials, the question is often propounded by the insurance company or the Courts, whether the case is one of spontaneous combustion or not? This is frequently very difficult to answer in a definitive manner, owing to the material having been entirely destroyed, or badly sampled, or not sent for examination in good time.

To enable the chemico-technical expert to arrive at a decisive opinion it is necessary that samples should be taken as soon as possible after the fire, and the following tests applied:—

(1) Specimens of the fibrous and fatty materials in the state in which they are treated in the factory, or kept in the storeroom. These must be tested for their liability to spontaneous ignition, both alone and in admixture with the fatty or other substances employed during their treatment.

(2) Specimens of the fibrous material must be taken from different spots at the site of the fire; wholly unaffected by the fire, partly charred, and entirely destroyed respectively.

(3) These samples must be kept apart and examined for their state of carbonisation, their fat content, and finally for the presence of spontaneous ignitable loading ingredients, dyestuffs, or extraneous admixtures.

(4) An examination must be made at the site of the fire as to whether the heaps of still externally unaffected masses of material are internally warm, singed, charred, or contain any glowing particles of fibre.

Special care must be taken in sampling to keep the different specimens by themselves, the samples being drawn from above, below, on the surface, out of the middle, and immediately sent for examination. Each sample should be of fair size, not less than  $\frac{1}{2}$ –1 lb. in weight.

In the investigations *in situ*, it is important to ascertain at what distance the materials were anteriorly situated from the nearest source of heat, and how they have been influenced thereby. The term “source of heat” applies to lighting arrangements, steam pipes, heating pipes, and eventually the rays of the sun.

If the interior of masses that are still intact be found to exhibit: (1) high temperature, (2) slight browning, (3) charring, (4) channels filled with carbonised material, then a tendency, at least, to spontaneous ignition may be regarded as proved.

The testing of the fats and oils should be directed to ascertain whether they are of animal, vegetable, or mineral origin, or mixtures of such.

Dyestuffs must be examined to see whether they are uniformly distributed, and whether or not they can have become partially detached from the fibres and formed into small accumulations. The failure to discover either fat or dangerous dyestuffs in the fibres is no proof that spontaneous ignition has not occurred, a handful of greasy fibre or dyed woollen rag being sufficient to start spontaneous ignition in a whole mountain of unoled fibre or textiles, and thus set the mass on fire. The

presence of traces of such greasy fibre or rag should be looked for in the masses left intact by the fire.

The smaller the traces of oil or fat discovered in the fibre, the more should attention be bestowed on the dyestuffs and loading adjuncts. In the case of silk especially (*q.v.*), but also in unoled cotton or wool, the presence of tannin and ferrous salts, certain aniline dyestuffs, inferior aniline oxidation black, diamond black, and dyestuffs containing chlorates or picrates, may incite spontaneous ignition.

For the dangers caused by disinfection and the expulsion of vermin from fibres and textiles, see *Disinfection*.

Specially high fire risk attaches to all decorative fibrous materials that have been exposed for a long time to the influence of the sun, or to stove and room heat, these gradually becoming desiccated and covered with dust to such an extent that the smallest spark, flame, or exposure to strong heat will suffice to set them alight. To this class belong curtains, old roller blinds, Makart bouquets (of dried grass, palm leaves, &c.), wall decorations of straw, paper, millboard, celluloid, &c. The most inflammable of all are Makart bouquets and varnished artificial pot plants, particularly when the latter are new.

## CHAPTER XXXV

### DISINFECTING AGENTS

#### 1. Disinfection

THE process of disinfection may be accomplished by means of heat, or by disinfecting agents. In the former event the risk of fire is small, it being impracticable to employ high temperatures when the articles treated are to be preserved. In fact, where it is a question of freeing an object from dangerous organisms and converting it into a new product, *e.g.* the disinfection and conversion of animal carcasses into fodder and fertilising substances, fat and glue, the temperatures employed do not exceed 320° F.

The employment of heat for disinfection must be carried out strictly in accordance with scientific discoveries as regards the temperatures necessary, since if this be disregarded and the operation performed at haphazard, great risks would be incurred. The various disinfection apparatus in use (*e.g.* those of Podewil, Henneberg, and Rohrbeck) are perfect in construction and working; and the same applies to those used in hospitals. More dangerous is the operation of disinfecting unsorted waste products that have been collected in all sorts of places and consist of any number of substances: rags, paper, cartridges, fibrous materials, textiles, bristles, hair, &c. These substances are not always free from oily or fatty substances of an inflammable nature, or from the accidental presence of matches, or other means of kindling fire, and from readily inflammable residues (in one instance gunpowder has been detected). In

such cases a low heat will suffice to actively excite spontaneous ignition or to set the material alight direct.

According to the character of the materials under treatment and the injurious organisms to be destroyed, the heat (mostly employed in the form of a current of steam) may attain 122°, 140°, 212°, and even as much as 320° F.; and at the same time, attention must be paid to the pressure of this steam, which at the last named temperature is as much as 6 atmos. When direct steam is used for disinfection the articles must be afterwards dried, an operation that may lead to ignition in the case of such easily kindled things as decorative and other articles filled with seaweed, wool, &c., unless the temperature be carefully regulated.

Disinfection with gaseous and other disinfecting agents is a far more risky process, these substances being often highly inflammable, some of them liable to ignite spontaneously, and a few even explosive.

The tendency of quicklime disinfectants to take fire of their own accord is dealt with under *Calcium*.

Many disinfectants are composed of readily inflammable mineral oils, tar and tar products, carbon disulphide, and benzol; the explosive hydrogen peroxide (carriers of oxygen always possess disinfectant properties), and bleaching powder (chloride of lime) are two very popular disinfectants, though not entirely free from danger of explosion (see description of both).

Disinfection by means of these agents increases the fire risk of the articles treated; and the process itself, which is frequently carried out with heated agents, is attended with danger from fire (see *Tar*, *Carbolic Acid*).

Amongst the disinfection processes occasionally exhibiting a high degree of danger, the author classes: the preserving of articles from putrefaction and decay, impregnation (in part), and the destruction of vermin in walls, beds, furniture, flooring, ceilings, textiles, fibrous materials, &c. Particular risk attaches to the use of insecticide solutions consisting of carbon disulphide (*q.v.*), since furniture, &c., treated with these remedies may easily take fire if exposed to flame, even though the disinfectant has only been dropped or squirted into the cracks.

Bleaching is analogous to disinfection, and may result in fire or explosion from the employment of such agents as hydrogen peroxide (*q.v.*), bleaching powder, carriers of oxygen, turpentine, or ozone.

To keep vermin (moths) out of large quantities of fibrous materials, textiles, furniture, furs, &c., the materials are frequently dusted over with naphthalene, or bags of naphthalene are hung up in the midst of them; and though naphthalene itself is incapable of producing any direct ignition, its vapours increase the inflammability of the materials, being given off at the ordinary temperature, impregnating the fibres and textiles, and thus enveloping them with a combustible vapour.

## 2. Hydrogen Peroxide (Hydrogen dioxide, Superol)

Sp. gr. 1.458. Boiling point 69.2°–85° C.

This syrupy liquid is one of the best disinfecting and bleaching agents known. In the pure state it is highly explosive, particularly in presence of dusty, rough bodies, metallic powders, when rapidly

moved or gently heated, in contact with acetone or any liquids that liberate volatile and inflammable vapours (benzol, carbon disulphide, ether). It is equally dangerous when in contact with chromic acid, manganese dioxide, or carriers of oxygen or ozone generally, *i.e.* resins, colophony, and ethereal oils.

Being itself a carrier of oxygen, it will feed a conflagration once started; it should be kept out of the way of all lights or burning bodies.

The method of preparation is dangerous; nevertheless it is pursued on a large scale by treating barium peroxide with acids. The resulting solution must be concentrated in a partial vacuum, and distilled, since it otherwise decomposes with explosion. Another method consists of warming explosive sodium peroxide at 400° C. in presence of air poor in oxygen; this process is more risky than the other. A third method is by treating potassium percarbonate with sulphuric acid or alkalis.

Fortunately, it is unnecessary to use hydrogen peroxide in a pure, undiluted condition, in which it would corrode or destroy everything. For disinfecting purposes it may be used in the form of a 3–5 per cent. aqueous solution, being readily soluble in water and evaporating concurrently with the water vapour.

It is specially used in the laundry, in the form of yellowish-white pastiles (Superol), which liberate oxygen in presence of cold water; as a cosmetic for bleaching hair, for bleaching wool, furs, or ivory; picture cleaning; as a chemical oxidising agent, and for the treatment of wounds in surgery.

When hydrogen peroxide is stored in a pure state, undiluted, the storage vessels must be coated inside with paraffin, this substance being unattacked by the peroxide. All contamination with dust, organic matter, &c., must be avoided, as increasing the danger of explosion during storage. Indeed, on account of this danger, hydrogen peroxide is often replaced by sodium peroxide.

An exceedingly dangerous solution of hydrogen peroxide in ether is known as Richardson's ether (*q.v.*). With acetone an extremely dangerous explosive compound (hydrogen trioxide) is formed.

Recently, hydrogen peroxide has been prepared in a crystalline state. The crystals are of a very dangerous character, exploding immediately on contact with spongy platinum, manganese dioxide, or peroxides generally. The crystals, or a 90–95 per cent. solution of same, will also produce immediate ignition in presence of mixtures of charcoal and magnesium powder. Lead dust, fibrous substances, and even wet sponge are ignited by these crystals, though iron powder is not except in presence of traces of peroxides.

### 3. Formaldehyde (Formic aldehyde, Methyl aldehyde, Formalin, Formol).

This disinfectant, a gas, is harmless in itself, but must find mention here because when used for disinfecting dwelling-rooms, clothing, furniture, stuffed animals, furs, &c., it must be prepared on the spot every time. In other cases it is used in the form of a liquid.

Gaseous formaldehyde is prepared by means of a spirit lamp filled with methyl alcohol, the flame of which heats a platinum gauze to in-

candescence. This accomplished, the lamp is extinguished, but the vapours continue to impinge on the glowing metal, which they retain in that condition without taking fire, but are themselves decomposed into formaldehyde, the vapour of which is disseminated through the air of the room.

This method is open to some objection owing to the character of the methyl alcohol; and, by reason of the irritating vapour, the room under disinfection cannot be entered during the operation. Furthermore, the considerable heat generated by the decomposition of the alcohol may cause the vapour of the latter to ignite if there is any draught or the gauze gets too hot, in which event the production of formaldehyde ceases. The heat of the spirit lamp may then cause an explosion of the hot alcohol, and lead to an outbreak of fire that remains undetected until too late.

To prevent the reignition of the alcohol, the lamp is fitted with a chimney; and above all, care must be taken to prevent the flame, in case of reignition, setting fire to any inflammable articles present.

Formaldehyde may also be employed in the state of solutions that liberate this substance as vapour when heated. The commercial 40 per cent. aqueous solution, known as formalin, is harmless; but the solution termed holzin is dangerous, wood spirit forming the solvent; when holzin contains menthol, it is called holzinol.

Sterisol (formaldehyde dissolved in a solution of milk sugar) is quite safe. On the other hand, in cases where water cannot be used formaldehyde is dissolved in benzol, which is naturally open to serious objection. Wherever formaldehyde is used, care must be taken to ascertain whether it is prepared direct by the decomposition of methyl alcohol, or employed in the form of a ready-made solution; in the former event all readily inflammable articles must be kept out of the way, and in the other case the kind of solvent must be specified.

## PART VI—DANGERS CAUSED BY AGRICULTURAL PRODUCTS

THE products here in question consist of :

1. Manures, (*a*) stall manure ; (*b*) artificial fertilisers ;
2. Fodders, (*a*) fodders in general ; (*b*) concentrated fodder ;
3. Crops, (*a*) for human food ; (*b*) for industrial purposes.

Since the products in classes 2 and 3 may be employed for a variety of purposes, they will be treated together.

### CHAPTER XXXVI

#### MANURES

##### 1. Stall Manures

The only place where this product becomes dangerous is in the fold (not in the stall or on the land), and then only when it has reached a certain age.

When solid and liquid excrement, intimately mixed with straw, sawdust, foliage, or peat, is shut off as much as possible from access of air, and left to itself, the two principal ingredients, dung and litter, acquire a more homogeneous character and finally decompose into a pulverulent mass.

These alterations are induced by chemical and biological processes ; the first stage is one of putrefaction, wherein the elements nitrogen and carbon, and the products ammonia, sulphuretted hydrogen, phosphoretted hydrogen, and hydrocarbons, are formed. By this process and the heat liberated and accumulated thereby, the mass of manure becomes so dried and loosened as to admit of air to the interior of the heaps.

The products, in so far as the same are not dissipated in the form of gases, now come into contact with atmospheric oxygen, with which they combine (oxidation), and the manure passes from the putrefactive to the rotting stage ; but, as in every process of oxidation considerable heat is generated, the resulting heat may accumulate to such an extent that, unless counteracted by efficient surface cooling, the more unstable putrefaction products may become carbonised, and the manure is " scorched." The temperature under these circumstances may attain 160° F.

When these internal processes are accompanied by external influences, such as exposure to hot sun, contact with glowing cinders, dry foliage or straw, accompanied by the formation of inflammable phosphoretted hydrogen from sawdust (*q.v.*), and if, furthermore, the manure heaps are high and large, then the increased heat may carbonise the dry matter, forming pyrophoric carbon, so that a feeble glimmer is produced, which, under favourable circumstances, may burst into flame.

Spontaneous ignition is of rare occurrence in stall manure, but is possible, and has actually happened, though it does not always arrive at an actual outburst of fire.

The first thing to do is to prevent spontaneous heating, which is a phenomenon adverse to the farmer's interests and prejudicial to the manure.<sup>1</sup> The best means of doing so are by giving proper attention to the manure heaps and providing them with a sufficiency of moisture, excluding the air, sheltering them from the influence of the sun, keeping away all heat-generating substances, such as ashes and cinders, regulating the size of the heaps, and carting the manure on to the land as soon as possible. When the heating has been prevented from attaining an objectionable degree—its entire suppression is impracticable—all danger of spontaneous ignition is obviated.

The tendency to heat varies considerably according to the class of excrement in the manure, that of goats and sheep being the hottest. However, since sheep dung is rarely, if ever, mixed with litter, but is trodden down very firmly and kept moist, no risk of spontaneous ignition is incurred in this case, though the conditions are different in the case of goat's dung, this being mixed with a large proportion of very dry foliage. Next in order comes horse dung, then that of swine (if mixed with litter), and finally that of cattle as the coolest of all.

The droppings of poultry form a hot manure, similar to that of sheep, but also heating without the risk of spontaneous ignition, owing to the absence of combustible litter.

An important part in manures is played by extremely minute micro-organisms, though the scorching of the heaps cannot be attributed to their activity, all that they do being to convert the mass into a combustible condition. According to Cohn, the activity of these bacteria is merely capable of raising the temperature to 158° F., at which point they perish, being unable to stand any greater heat.

When the manure heaps are of very large dimensions, this bacterial activity becomes of greater importance to the preliminary stages and progress of spontaneous ignition. For further particulars see *Spontaneous Ignition of Fodder*.

## 2. Artificial Fertilisers

Of artificial manures the name is legion, but we will confine ourselves to the following:—

(a) *Stassfurth salts* (potash salts, chloride of potash, carnallite, kainit, kieserit, magnesia salts) are entirely safe and incombustible.

<sup>1</sup> *Translator's note.*—This is perhaps hardly accurate, a certain degree of heating being necessary to secure the proper rotting of the manure. The extent to which this should be allowed to continue depends on a variety of circumstances. At any rate, the *control* of the process is desirable in all cases.

(b) *Thomas slag*, Thomas meal (phosphate of lime manures). This is incombustible, but contains about 50 per cent. of quicklime (*q.v.*). Some risk is incurred when these fertilisers are bagged damp and stored in high heaps, since the heat generated by the slaking of the quicklime may be great enough to set fire to the bags in which the fertiliser is packed. A second danger is incurred when Thomas slag is mixed with combustible, damp organic adjuncts, like guano, dried blood, &c., the heat generated by the action of hygroscopic moisture on the quicklime burning the organic adjuncts as well as the bags. Under favourable circumstances the heat becomes so great as to render the mass almost incandescent.

(c) *Phosphatic manures*, guano phosphate, crude phosphate, bone phosphate, Baker phosphate, Mejillones phosphate, precipitated phosphate. These are free from any dangerous properties. They are, however, not used direct, but only after treatment with sulphuric acid, in which condition they are known as dissolved phosphate; or,

(d) *Superphosphates*. These fertilisers are often mixed with nitrogenous manures, in order to obtain a product of improved composition, nitrate of soda or sulphate of ammonia being used for this purpose. In the latter event the product is known as ammoniacal superphosphate.

The superphosphates and their mixtures may be regarded as free from danger, provided they have been properly manufactured. This is not always the case, owing to carelessness in adding the nitrate of soda. Thus, if some uncombined sulphuric acid be left over from the decomposition of the raw phosphate, and nitrate of soda be added at once, a very powerful reaction is set up, the acid decomposing the nitrate of soda, whereupon the liberated nitrous fumes nitrate the bags and the organic matter present and impart a tendency to take fire (see *Nitration*). The author has had two instances of this kind put before him for investigation, and ascertained the cause of the by no means inconsiderable outbreaks of fire to be: incomplete combination of the sulphuric acid with lime, imperfect drying of the superphosphate, and prematurely adding the nitrate of soda and bagging the product. The outbreaks occurred in 20–24 hours after the arrival of the manures.

Such cases of spontaneous ignition in superphosphates are impossible where the process is properly performed, the laws of chemical reaction being then strictly observed. On the other hand, this danger is always imminent when, for the sake of economy, the farmer buys the ingredients separately and mixes them at home, little attention to chemical reactions being paid in the farmyard, and mixing in any proportions being looked on as sufficient.

The risk of spontaneous ignition can, however, be obviated by using sulphate of ammonia for mixing, instead of nitrate of soda.

(e) *Nitrate of soda*, or Chili saltpetre, possesses the usual dangers attaching to nitrates (*q.v.*). In addition to the risk mentioned under (d), it exhibits the great inconvenience of making the bags highly inflammable. In damp weather it absorbs moisture, the solution penetrating the fibres of the bag so that the smallest spark is sufficient to cause these impregnated Chili bags to glimmer.

Hence old or full Chili bags are very dangerous articles. They should be well cared for and not used again (at least for phosphate

manures) until they have been thoroughly washed, which should be done as soon as they are emptied. The chief danger lies in the fact that they often continue to glimmer for some time unnoticed, until an outbreak of fire, highly dangerous to farm premises, occurs.

(f) *Sulphate of Ammonia* is harmless in itself, but exhibits the peculiarity of very strongly heating straw that has been repeatedly immersed in and saturated with the dissolved salt (see *Ammonia*).

(g) *Lime*, quicklime, burnt lime, agricultural lime, is very dangerous in presence of water, with which it enters into combination accompanied by the generation of strong heat (up to 800° C.), and is therefore a source of danger to all readily inflammable substances, such as hay and straw (see *Calcium*). Now, these materials are often mixed on farm premises for the preparation of manure, an operation that may lead to violent spontaneous ignition. The substance mixed with quicklime are: fowl droppings, slaughter-house waste, sinews and blood. Experiments conducted with slaughter-house waste on a large scale (12½ tons at a time) gave the following temperatures within a very short time: with 6 per cent. of lime, 140° F.; with 12 per cent., 140°–158° F.; with 36 per cent., 203° F. This last heap broke out into flame very soon after reaching the above temperature, but was soon extinguished owing to the low combustibility of the materials; in presence of hay or straw a large fire would undoubtedly result under similar circumstances.

The spontaneous heating of mixtures of lime and organic matter does not begin until the mixture has been moistened.

(h) *Artificial Guano*, mostly composed of flesh and fish manure (fish guano), is packed very tight and in a dry state, and stored in large heaps. So long as these conditions are maintained, the degree of spontaneous heating remains below the danger line; but practical experience has shown that the demolition of such heated masses may cause the temperature to rise to such an extent that the exposed mass chars and even commences to glimmer. It is not improbable that some part in this phenomenon is played by the fat intimately incorporated with the flesh composing these artificial guanos.

The risk of spontaneous ignition in artificial manures is, after all, a very natural characteristic, since, in order to fulfil their purpose of becoming absorbed by the delicate rootlets of young plants, or converting the solid constituents of the soil into plant food, these manures must possess a specific chemical nature and brisk chemical activity, so as to be sensitive to feeble reactions.

For this reason they do (and must) not consist of inert ingredients; and it is not unnatural that such substances should, when improperly handled, exert their chemical powers in the wrong direction and expend a portion of their activity in generating heat at the wrong time and place.

Hence, despite their earthy, often black and unsightly, appearance manures must not be regarded as dead, lifeless earthy masses, but should be treated as chemicals capable of reaction. Especially must a certain amount of care be exercised in mixing them, since these mixtures enter into mutual chemical reactions, generate heat, and are therefore twice as dangerous as the simple manures.

Both on account of the loss of fertilising power and of the imminent risk of fire occurring when artificial manures are mixed in an unintelligent

manner, the observance of the following rule is to be recommended. The undermentioned substances should not be mixed or stored together :

1. Meat meal, blood meal, stall or pit manure, guano, fowl droppings, ammoniacal manures, } with { quicklime, agricultural lime, Thomas slag or Thomas meal.
2. Dissolved phosphates, *i.e.* guano, Mejillones, Baker-, or bone superphosphates containing sulphuric acid, } with nitrate of soda.
3. Thomas slag meal, quicklime, agricultural lime, } with the manures mentioned under 1.

Should such mixtures be required for manurial purposes, they ought to be conveyed to the land as soon as prepared.

The losses sustained by fertilisers in consequence of spontaneous heating or fire are very divergent, and may be either of a chemical character or physical.

An efficient manure must possess certain physical and chemical properties in conjunction, the presence of the most valuable chemical properties being unavailing when the requisite physical characteristics of fineness of division, solubility, and pulverulence are partly or wholly lacking.

Manures.	Losses sustained.
Nitrate of soda, Sulphate of ammonia, Peruvian guano,	Completely decomposed by heat, and rendered worthless by loss of nitrogen.
Ammoniacal superphosphate, blood meal, flesh meal, and bone meal,	Sustain loss of nitrogen, ammonia, organic matter; the solubility of the phosphates retrogresses; the mass becomes lumpy and can no longer be distributed in a uniform manner.
Baker-, Mejillones-, and other non-nitrogenous phosphates,	Suffer no direct loss of manurial ingredients, but the phosphoric acid loses at least half its value owing to diminished solubility, and the mass ceases to be distributable.
Quicklime, agricultural lime, Thomas slag, Raw phosphate, Potash salts, Stassfurth salts,	Heat does not produce any loss of manurial ingredients, but the pulverulence, which is a prime condition for their fertilising action, is lost; they ball together and must be reground before they are fit for use.

The addition of water to fertilisers renders them difficult of distribution, and also dissolves out the most valuable constituents, more especially the soluble phosphates in superphosphate, the potash in kainit and allied salts, and the nitrate of soda in Chili saltpetre. Adding water to quicklime makes it lumpy and diminishes its power of loosening the soil, the chief reason for employing this fertiliser.

In few branches is a knowledge of the internal reactions of mixtures so essential to the prevention of spontaneous ignition as in the manufacture of artificial manures, since ignorance (which certainly is only encountered in small works and on the farm) may easily lead to heating, fire, and the spoiling of the materials.

In order to arrive at a proper appreciation of the proposed risks it is highly desirable to discontinue the general terms "manures" or "artificial manures" in describing the objects of insurance, and to require fuller details as to composition, especially as regards the presence or absence of nitrate of soda. The rigid separation of mutually dangerous fertilisers during storage should be insisted upon; nitrate of soda and quicklime being kept apart from other manures, and also from the sulphuric acid used in the preparation of superphosphate; quicklime and Thomas slag must be protected from moisture, even that arising from the ground.

Chili bags must be washed as soon as emptied. Where nitrate of soda is used, open lamps and fires should not be allowed, except under careful management; and all means of producing ignition must be carefully excluded from store- or workrooms where the timbers, panelling, or flooring may have become impregnated with nitrate. Fertilisers that have become wetted by flood or subsoil water must be removed at once and dried, otherwise spontaneous heating may occur; this is particularly the case with fertilisers containing quicklime and Thomas slag. Practical experience has shown that wet Thomas slag meal may heat spontaneously to the point of incandescence.

When fertilisers have been quenched with water an immediate strong superficial cooling, or drying, is as essential as in the event of wetting from other causes.

The manufacture of artificial manures may become a dangerous process when any of the inflammable fat solvents (benzol, ether, carbon disulphide) is used for extracting fat from the raw materials, as is done more particularly in the case of bones, for the production of bone fat and steamed, de-fatted bone meal.

In other cases the treatment pursued is merely one of decomposition with sulphuric acid or high pressure steam, followed by drying at an air temperature of about 250° F., and reducing to powder. In utilising carcasses and slaughter-house offal by means of the Podewil, Rohrbeck, or Henneberg system, &c., a steam temperature of 250°-320° F. is employed; in this event the recovery of the fats is unattended with danger, no solvents being used.

## CHAPTER XXXVII

### FODDER

#### 1. Spontaneous Ignition

AGRICULTURAL fodders, such as grass, hay, clover, straw, bran, chaff, chopped up materials, cereals (wheat, barley, oats, rye), rice, maize, leguminous seeds (peas, beans, lentils, lupins, vetches), oil seeds (rape,

poppy, linseed), present no danger when in a fresh state, owing to their low combustibility, except in the case of hay and straw. On the other hand, they are highly inflammable when dry, a small spark being sufficient to set them on fire. The floating dust they yield when ground forms a highly explosive product, especially when this dust is derived from impurities from the grain, skins, husks, &c.

In two other eventualities can these substances also give rise to danger: (1) when piled up in large heaps, or tightly packed in bins, &c., whilst still in a fresh state; and (2) if allowed to get wet when in the dried state, and then stored for some time in this damp condition. In either case an opportunity is afforded for the occurrence of far-reaching chemical changes within the mass, the latter then becoming decayed, heated, charred, and finally falling a prey to combustion. These changes may proceed to the fullest extremity, or be arrested at any intermediate stage; but, owing to the diversified character of these agricultural products, it is very difficult to decide in any case whether the limit attained is merely one of simple decay by wet, heating, charring, or whether the product is ruined by spontaneous ignition and combustion.

In many instances, however, a solution is required of the problem whether the damage is one of mere spoiling, or whether the case is one for compensation under the insurance policy. The only way to arrive at a decision on the point is to have samples taken in good time and examined immediately, the report being drawn up on the results obtained and the information afforded by eye-witnesses. However valuable the testimony of such eye-witnesses may be, it is never quite reliable in settling the question whether a case is one of combustion or not. There are so many phenomena that may deceive persons destitute of chemical knowledge into the belief that a case is one for compensation, that the question cannot be settled without the weighty evidence of science.

The ease with which the inexpert may be deceived is clearly shown in connection with the estimation of temperatures. Such a person examining a heap of heating matter is likely to assume, from the heat given off, that a fire is actually raging in the interior of the mass, whereas in reality the temperature may be only 120°–160° F., or very far below that of true combustion. This faulty estimate is the more likely to arise where the heap in question—say 25–50 tons of bran—is indoors, and the disengaged heat has no opportunity of being dissipated.

The mouth is scorched by soup at a temperature of 120° F., or the finger scalded by immersion in water at the same temperature, the pain produced being as intense as that from contact with a match flame with a temperature of 600°–1100° F. Moreover, we can pass the hand through a very hot flame (600°–1100° F.) without feeling any pain, though merely taking hold of a pan heated to 160°–175° F. causes serious discomfort. If we place a foot on a pile of heated hay, at a temperature of 120° F., the heat soon becomes insupportable, whereas it feels only moderately warm to the hand, the more sensitive foot magnifying the sensation three or four times in comparison with that experienced by the hardened hand.

The organoleptic reaction being so deceptive, the only reliable method of estimating temperature is by the thermometer.

In other directions too, the inexperienced are liable to fall into error.

For instance, nearly all kinds of agricultural products that are undergoing, or have already sustained, decay exhibit whitish masses of fungi, which present the appearance of ash resulting from combustion. On the other hand, when the mass is blackened, the inexperienced eye attributes this appearance to charring, whereas it is merely the result of extensive fermentation (empyreumatic products). This is often noticeable in grain. The rotting heaps may give off a burning smell, like malt or burnt milk; but this smell, which is produced at temperatures as low as 140°–170° F., arises solely from fermentation products decomposed by spontaneous heating.

Peat, again, has a burnt look, being brown and often black, and yet the temperatures to which it has been exposed have never risen above 122° F.; and it frequently happens that the water vapour rising from a heap of decaying matter, and coloured brown by volatile fermentation products, is mistaken for smoke.

All these phenomena speak in favour of fire, and if sworn to by witnesses in court may convince a judge, whereas in reality they have all been produced by a process of spontaneous decay, at temperatures between 165° and 195° F., and have nothing in common with a case of fire in which the insurance company is liable. It is therefore the task of the chemist to throw the proper light on this testimony, and investigate and sift it from the chemical standpoint.

In examining the problem “decay *versus* spontaneous ignition,” the following points should be borne in mind, no matter what the class of agricultural produce in question:—

Stage 1. Fermentation, incited by micro-organisms, may generate a temperature of 132° F.

Stage 2. Charring. This occurs at 132° F., but does not extend to the mass of the material; the cellulose is not affected, the action being confined to the products of fermentation, which are browned by the existing temperature (132°–140° F.) and char, thus presenting the appearance of products of combustion, without really being such. The temperature may rise to about 212° F.

Stage 3. From 212° to 265° F. the chemical reactions commence, which constitute the initial and intermediate stage leading to spontaneous ignition.

So long as the first two stages prevail the case is only one of decay, however closely the reactions and products may externally resemble combustion. The limits of the spontaneous ignition stage are formed by the chemical processes occurring at 212°–265° F., and it is only when this latter temperature is exceeded that true combustion, and therefore a case for compensation, can be said to have taken place.

According to the nature of the materials, method of storage, age, moisture, influence of the sun, &c., the phenomena of decay and spontaneous combustion in agricultural products may exhibit considerable variation. Similar fluctuations may occur in the external appearance of the products, and in the heat radiated from the heaps; but the temperature limits are fairly constant, with merely a slight range of variation.

Thus, biological phenomena occur up to 132° F.; carbonisation of the biological products at 132°–212° F.; charring of the less stable subsidiary constituents of the mass (fat, albumin, carbohydrates) at 212°–265° F.;

spontaneous ignition, charring of the celluloses themselves, *i.e.* actual combustion, at 265° F.

The augmentation of temperature is due to the fact that the heat generated in the mass is prevented from escaping, and therefore accumulates and is stored up therein.

The following table gives further information of the details of the various stages up to the point of spontaneous ignition:—

Substances giving the initiative.	Mode of activity exhibited.	The process gives rise to :
1. Vegetable cells.	Vitality, respiration.	Increased temperature in the mass (up to 122°–132° F.). (See 2.)
Spores of Fungi.	Growth of micro-organisms.	Partial desiccation of the heap.
Seeds.	Production of embryo plants.	Formation of products of vitality and decomposition. (See 2.)
2. Warmth and desiccation.	Together decompose the volatile compounds and microbial products (see 1).	Nitrogen and hydrogen gas are liberated. The mass turns brown, carbon being formed, along with empyreumatic substances. (See 3.)
3. Empyreumatic substances.	Deposit finely divided carbon.	This carbon (charcoal) attracts oxygen.
4. Finely divided carbon.	Absorbs and condenses oxygen in its pores.	Further generation of heat (132°–212°, or even 266° F.), the sensitive empyreumatic products being decomposed, the mass desiccated, and internal air conduits formed.
5. Desiccated masses, Carbon, and air passages.	Access of air, increased absorption of oxygen by newly formed carbon.	Temperatures above 265° F. Formation of pyrophoric carbon. Incipient carbonisation of celluloses. Chemical modification of same. Eventual ignition and actual fire.

1. These are the biological processes.

2. Influence of heat on the primary products.

3 and 4 are the initial processes of (low-temperature) carbonisation, which, however, affect merely the biological products and less stable constituents (albumin, carbohydrates, and fat), leaving the chief ingredients unaltered.

5. These are the chemical processes (high-temperature carbonisation).

It should also be borne in mind that even small amounts of agricultural products, gathered or stored in a damp state, or wetted by flood-water, rain, &c., may suffice to set up decay or spontaneous ignition in large heaps of the same products in a dry state. A bag of damp grain, a bundle of wet hay, a heap of sprouting corn, are able to damage the best and most carefully gathered products.

If the moisture gain access from above, through a defective roof or

an overlying stratum of wet substances, the danger is less intense. In such cases the cause of the decay or combustion can be traced by the presence of damp or spoiled material on the surface of the heap. A more dangerous condition is produced when the moisture has been imparted from below or from the centre of the mass; in the first place, the danger is recognised too late; and, secondly, it is difficult to prove that the entire heap has been spoiled by the presence of a small quantity of damp material, for the simple reason that this damp material is the first to be altered by spontaneous heating and disappears from the ken of the investigating chemist.

An equal degree of danger to the heaps is produced by the presence of upright wooden pillars or props, of a resinous character or painted over with spirit- or oil-paints. Timbers of this kind, which are very sensitive to the action of heat (see *Wood*), form as it were natural flues for the heat generated in the mass, since the materials never lie so closely together in the vicinity of these timbers as they would do otherwise. The constant flow of heat to the common centre formed by the timber acts upon the latter in the same way as a source of gradual heat or a steam pipe would do. Furthermore, the flow of heat is accompanied by moisture, which, in collecting round the timbers, may moisten the surrounding materials sufficiently to instigate the processes leading to the decay and eventual spontaneous ignition of the same. The danger incurred by the presence of such timbers increases in proportion as the usual practice is followed of piling up the heaps thickest against the timbers.

Instances have occurred where wooden pillars, standing in the midst of heaps of wet, spoilt grain, bran, or hay, have themselves been charred before the surrounding materials attained the stage of spontaneous ignition.

On this account it becomes necessary to make such timbers flame-proof. On the grounds of general safety, moreover, it is just as essential to accurately control the internal temperature of the heaps, the store being visited every week in order to detect the appearance of any smell, especially that of fresh bread, empyreumatic substances or herring pickle. When high temperatures or suspicious smells are observed, care must be taken to have the store properly ventilated, the heaps turned over to ensure proper surface cooling, and the pillars and corners laid bare. Should the internal temperature already attain the critical point ( $140^{\circ}$  F.), the top portions of the heap must be removed in a uniform manner, the sides being left untouched, otherwise a dangerous admission of air to the interior may result.

All stores where agricultural products are kept in large bulk must be visited at least once or twice a week. To keep such a store locked up for a month at a time, with only a single visit (as is sometimes done), is a proof of negligence, which is the greater and more reprehensible when the owner is aware of the changes and alterations to which agricultural products are liable; knowledge which must certainly be possessed by every farmer, corn merchant, &c.

## 2. Hay

In the fresh products: grass, hay, clover, maize leaves, millet leaves, turnip tops, foliage, &c., the vegetable cell retains its vitality for some

time after the plants have been cut; respiration continues and is accompanied by the generation of heat. To this heat must be added that produced by the vital activity of the never-failing spores and germs of micro-organisms; and finally, since all agricultural products contain seeds, the latter in germinating also develop heat.

None of these sources furnish heat that is appreciable so long as the products are spread out to dry, since no accumulation of heat can occur under such conditions. So soon, however, as the materials are piled up in such a manner as to retain the moisture present (a prime essential for the inception of the subsequent processes), then the escape of heat is prevented, though it remains harmless while a sufficiency of moisture is retained, or it is afforded a timely means of escape, or finally, so long as the mass is pressed tightly enough to prevent the penetration of air to the interior. These circumstances have been utilised for the preparation of brown hay (*q.v.*).

The temperatures produced in heaps of fresh grass, clover, leaves, &c., differ considerably; bedewed substances generate greater heat than if wetted by rain, a circumstance attributable to the small percentage of nitric acid and ammonia present in dew.

Prof. Cohn found that the temperature in heaps of fresh grass rose from 64.4° to 86° F. within 24 hours, and to 134½° F. within a few days; Prof. Maerker records 125½° F., but admits that a temperature of 212° F. may be produced in fresh hay. The highest temperature of all, namely, 572° F., was observed by Prof. Ranke, which temperature, however, belongs to the stage of spontaneous ignition.

Loennecker detected a temperature of 104° F. in a large haystack 10 days after erection, but only 89½° F. in places where the hay was loose; within the next few days the temperature rose to 176° F., whereupon carbonisation ensued, and within 40 days spontaneous ignition occurred.

No definite rules can be laid down for the storage of grass, clover, or hay, &c.; but in general, observation of the following precautions should suffice to prevent the risk of spontaneous ignition:—

The material harvested should be free from vegetation moisture, and from dampness caused by dew or rain. Should bad weather necessitate the material being heaped up in a damp state, it must be repeatedly turned over and loosened, to prevent the accumulation of heat on account of compression. The barn, &c., should not be packed right up to the roof, but a sufficient space left for ventilation and proper surface cooling.

Should, from any cause, this troublesome manipulation be found impracticable, the material should be used for the preparation of ensilage, or brown hay, the fresh grass (cut into coarse chaff if necessary) being placed in pits or heaps. Care must be taken to follow the instructions precisely, or the materials will be liable to rot or take fire.

No silo or stack should contain more than 20 ordinary loads; the grass must not be wet, though it may contain up to 75 per cent. of vegetation moisture, and may even be dew damp. The building of the stack or packing of the silo must be effected by degrees, fresh quantities not being added until the previous lot has cooled down and the mass ceases to exhibit any accession of temperature, this being controlled by a stack thermometer.

The temperature must not be allowed to rise above 122° F. during

these operations. All corners and cavities should be filled up properly, a circular form being preferable for the stack or silo. The mass should not be stamped down or pressed, otherwise than by its own weight, during the building or packing process. The incorporation of extraneous substances, like straw, turnip tops, beet leaves, &c., which would disturb the uniformity and closeness of the mass, is permissible only when the same are chopped small; on the other hand, strewing with coarse salt is advisable.

The bottom of the stack or silo should not be exposed to ground water or drainage from the outside.

When the twenty loads have been put in position the stack or silo should be well covered with boards, &c., and then, when it has ceased to sink to any considerable degree, should be weighted with stones, &c. The sole rule essential for these stacks and silos is that they must be entirely free from cavities and the penetration of air, otherwise they will rot and take fire.

The processes operating in these masses are as follow:—

Heat is generated, by cellular activity, within the mass of fresh vegetable material, and this heat favours the development of innumerable lactic acid bacteria, which produce lactic acid (hence the name “sour hay” for silage), and perish at 104°–122° F. The heat must have escaped and the bacilli have perished before a fresh layer of material is placed on the heap; otherwise the lactic acid will be destroyed, and the fermentation will proceed further, to the loss of the owner. When the process is properly performed the material becomes charged with lactic acid, which acts as a preservative, and the fodder will keep good for a year. When all is in order the danger of spontaneous ignition will be non-existent by the end of the first three months.

Before such a stack or silo is accepted as an insurance risk the insurer should ascertain, if possible, whether at any time during the building or within the three-months limit the temperature of the mass has exceeded 140° F. In such event there is still risk of subsequent rotting or spontaneous ignition, though the latter phenomenon will not be attended with flame.

It may be mentioned that brown hay is sometimes made in small stacks or heaps by the application of mechanical pressure. In such case the possibility of decay is increased by the number of the heaps, the more so because any one of them in course of decay may incite the same tendency in others with which it is associated.

### 3. Grain and Seeds

Like grasses, the various grain and seeds are subject to spontaneous decay and heating, though less liable to spontaneous ignition, this latter condition being of rare occurrence. In this case the principal part in generating heat is played by the seed germs (embryo), for though bacterial germs furnish heat up to a temperature of 104° F., the bulk of the heat is generated by the respiration of the *germinating* seeds, which are then said to “heat.”

The tendency to heat on the part of damp, unripe, and sprouted grain and seeds can be counteracted by drying, ripening, thin spreading and turning (not, however, during damp weather). Where heating is

likely to be injurious to the seeds the heaps should not be more than 4-6 inches in depth, and efficient surface ventilation must be provided. Later on the thickness may be increased to 16-20 inches. A very good plan for preventing heating is to place quicklime in open pans between the heaps of wet, spoiled grain (about 2 cwt. of lime to every 5 tons of grain). When the lime has become charged with moisture it can be used as a fertiliser.

During, and even before, heating the grain assumes a dark colour, which gives it the appearance of a charred mass, though merely due to the deposition of fine carbon from the decomposition of empyreumatic products, the carbonisation of the seeds or their husks being out of the question at this stage. This coloration, which is often quite black, may at the first glance produce the erroneous impression that an actual fire has occurred, and that the case is one for compensation. If, however, the seeds be tested with water and alcohol, the husks will appear in their natural colour again (white or yellow), which would not be possible if they had actually been scorched by fire.

Seeds that have been stored in bins and pits, under water, and have rotted, may give off inflammable gases. During the first four days the innocuous gases, nitrogen and carbon dioxide, are liberated; but, after about a week, methane (3-4 per cent.) and hydrogen (37-40 per cent. of the volume of gas) make their appearance. These gaseous mixtures being inflammable, and explosive in presence of air, it is very dangerous to enter or illuminate the pits, bins, &c., with open lights. Decaying brewers' grains behave in a similar manner.

For certain industrial purposes it becomes necessary to expose grain, starch, or flour to temperatures almost sufficient to produce pyrophoric carbon, *e.g.* kilning malt, and the production of colour malt, preparations of roasted flour (for confectionery), malt coffee, coffee surrogates, &c. The temperatures here in question amount to 150°-212° F. (or 750° F. with superheated steam), and the work is not without danger, the roasting being often performed quickly and producing considerable charring, which may render the substances pyrophoric.

The puzzling outbreaks of fire at one time prevalent in kilns were due to pyrophoric carbon, and are now of rare occurrence with the improved kilns in use.

To obtain a colour malt of high colouring properties the malt is mixed with about 6 per cent. of glycerin and exposed to a kiln heat of 390°-465° F. The glycerin acts as a preservative, by preventing the malt from burning; nevertheless, the temperature should be carefully watched.

Altering the shape of seed or grain, for use, or extracting one or more of the constituent substances, will not destroy the tendency to heat or take fire spontaneously. This tendency remains in the various members, *e.g.* the crushed grain, bran, skin, husk, &c., and in even greater degree than before the protecting influence of the integument was withdrawn. Furthermore, the various portions of the disintegrated grain generally form more compact masses than the original oval seeds, &c., which never lie so closely together, and therefore cannot retain heat so well as the bran, husks, &c. A considerable influence is also exerted by the plant germs which, even when separated from the seed, begin to evince vital activity, accompanied by an abundant liberation of heat.

Conditions that do not greatly favour the development of spontaneous ignition in grain while intact, become more likely to foster it in the supplementary constituents. As in the case of the grasses and seeds, the first incitement to the series of processes leading to decay, heating, and fire, is an access of moisture from above, below, or within. Other factors contributing to the same result are: heaping the materials to a thickness of 10 feet or more; neglecting to turn and aerate the heaps or ventilate the storage room, shut up for months at a time.

Parts of plants that are chiefly of a strawy or husky character are less liable to decomposition or spontaneous heating, their smoothness and poverty in moisture and food constituents rendering them less favourable media for the growth of micro-organisms. The development of the latter is suspended, and consequently the preliminary heat they furnish in other cases is here lacking (*i.e.* in straw, chaff, husks, and substances like seaweed). The preliminary condition for spontaneous heating being absent, the ignition stage is difficult to attain. On the other hand, these substances exhibit a correspondingly greater degree of inflammability and liability to direct ignition.

The spontaneous ignition of straw and analogous substances is, however, by no means impossible, and in fact may readily ensue when the straw, &c., is "dirty" (*i.e.* full of weeds), since the weeds dry far more slowly than the straw itself, and still contain vegetation moisture when stacked. Such dirty straw is specially liable to take fire of itself, particularly when it is much damped or wetted by soil water, rain, or other cause.

Danger may arise in straw, &c., in still another fashion: when repeatedly treated with ammonia water the straw will heat (212° F.), and if then piled in heaps may fall a prey to spontaneous ignition. The same thing happens when straw is treated with strong nitric acid (see *Acid Carboys*), and in presence of quicklime it takes fire when wetted. Finally, like wood, exposure to the influence of heat from steam or other hot pipes for a long time will render straw liable to ignite spontaneously.

Of other agricultural products, mention must be made of the following:—

#### 4. Hops

By the agency of wind, or contact with the soil, hop cones become infested with a fission fungus, which sets up, in the pressed bales (pockets), a fermentation accompanied by an accession of temperature; the consequence is that the hops decay, char, and may finally take fire spontaneously. Hops that have been gathered damp, or become so later, are more liable to this danger than dry hops or such as have been sulphured on the kiln. The only remedy is to carefully watch the internal temperature of the bales, and to open them and re-dry the hops with sulphur should the heat increase to any considerable extent.

Moreover, hops contain a resinous constituent, lupulin or "hop flour," which plays an important part, inasmuch as should it accumulate in any part of the pockets and get damp, it exhibits a tendency to spontaneous ignition. This is a matter of rare occurrence, but one difficult to remedy.

### 5. Tobacco

When tobacco is not sufficiently aerated during the fermentation process, it may heat spontaneously to the point of carbonisation. The same thing happens when it is tightly packed on ship-board in a damp state, or when the fermenting heaps are piled up so high that the surface cooling is insufficient to keep down the internal temperature.

It is very seldom that tobacco will heat so as to actually take fire, the material being difficult to kindle, and for the most part merely glimmering. However, it easily chars, and even the slightest degree of carbonisation in tobacco of any kind is quite as bad as combustion and destruction, since it entails the disappearance of the valuable aroma.

### 6. Molasses Fodder

Of the concentrated fodders, mention should be made of that prepared by mixing molasses with oily and starchy foods, like palm kernel cake, poppy cake, rape cake, ground-nut cake, and linseed cake. The product is liable to heat in a high degree, and even take fire, if piled in high heaps, damped, tightly packed and stored in a warm place, especially in the vicinity of heating apparatus or close under a roof in summer.

This heating is confined to molasses fodder rich in oil and meal, and need not be feared when the adjuncts are technically oil free, such as dried beet slices, bran, husks, brewers' grains, potato pulp, peat, chaffed hay, or straw. Whether any heating occurs when maize is added has not yet been ascertained.

# PART VII—DANGERS PRODUCED BY FATS, OILS, RESINS, AND WAXES

## CHAPTER XXXVIII

### FATS AND OILS

#### 1. General Remarks

By the term "fat" we understand mixtures of organic compounds consisting of glycerin and fatty acids (= glycerides), all of similar elementary composition and possessing certain characteristics in common, though differing considerably in physical properties. A distinction is drawn between:—

- |                          |  |
|--------------------------|--|
| 1. <i>Animal fats</i>    | { solid = tallow,<br>semi-solid = butter, lard,<br>liquid = train oil, |
| and                      |  |
| 2. <i>Vegetable fats</i> | { liquid = oils,<br>solid = cocoa-butter.                              |

The other so-called oils, such as mineral oils, tar oils, and ethereal oils have little or nothing in common with the true fats; chemically speaking, they are quite different, and merely exhibit certain physical properties analogous to those of the fats proper.

Sometimes a distinction is made between fats and oils, such as are solid being called fat, whilst those that are liquid are named oil. This is inadmissible, since all of them are fats, and the term oil merely applies to a class of fats that are liquid at the ordinary temperature.

A characteristic property shared by a number of vegetable fats is their tendency to pass over into a resinous or varnish-like substance when exposed to the air, which property enables them to be used as paints. Such fats are termed "drying oils," and include cottonseed oil, hempseed oil, linseed oil, nut oil, and castor (*ricinus*) oil. The others are known as "non-drying" oils, a class represented by olive oil, rape oil, cameline oil, beechnut oil, ground-nut oil, and almond oil.

This difference, however, is without influence on the general fire risk of the vegetable fats.

All fats consist of: carbon, about 74–79 per cent.; hydrogen, about 11–12 per cent.; and oxygen, 10–13 per cent.; these three elements

forming the two main constituents of which the fats are composed, viz. glycerin and fatty acids. The differences exhibited by the various fats are due to the quantity, nature, and proportion of these two components.

In the animal fats, both compounds are completely combined, in a chemical sense, and form a neutral substance; but in the vegetable fats this neutral substance is accompanied by free fatty acids. The most important fatty acids are: palmitic acid, stearic acid, and oleic acid, also called palmitin, stearin, and olein respectively for short.

Where palmitin and stearin predominate, the fat is more solid in character, but where olein prevails it is more liquid (oil).

All fats may be decomposed into glycerin and fatty acids by the action of alkalis (caustic potash or soda), lime, acids, or steam, the process being termed *saponification*. When steam is used, very high temperatures are employed (480°–660° F.).

Fats exhibit fire risk at the ordinary temperature, and explosion risk at temperatures above 500° F. The chief dangers are:—

1. Though in themselves fats are not easily kindled, and are unflammable at the ordinary temperature, they nevertheless, when permeating other substances, impart to these latter a great tendency to inflammability and combustibility, fibres and similar substances even becoming liable to take fire spontaneously under these conditions (see *Impregnation of Fibrous Materials with Oil*).

2. Since all fats melt at comparatively low temperatures (maximum 125° F.) and become liquid, they greatly help to spread flame and transmit it to other substances.

3. Burning fats generate great heat, and are difficult to quench.

4. This heat may liberate explosive vapours and gases from contiguous masses of fat that are not yet alight. Burning masses of fat may be characterised as explosive, and such fires mostly culminate in an explosion.

5. Fats give off vapours at high temperatures (480°–580° F.), which vapours take fire spontaneously when heated to 18°–20° F. above their temperature of formation. In presence of oxygen, or a mixture of oxygen and air, the vapours explode (see Table VII., Appendix).

In all these respects the risks of animal and vegetable fats are identical, except that as regards the spontaneous ignition of fibrous materials the vegetable fats are the more dangerous. If, however, the animal fats are rancid, they become more dangerous than pure vegetable fats.

At the following temperatures the oils specified will go on burning without a wick:—

Olive oil . . . . .	at 662° F.	Linseed oil . . . . .	at 662° F.
Rape oil . . . . .	„ 662° F.	Engine oil . . . . .	„ 275°–445° F.
Hempseed oil . . . . .	„ 329° F.	Spindle oil (light) „	505½° F.
Poppy oil . . . . .	„ 662° F.	„ (heavy) „	550½° F.
Sesame oil . . . . .	„ 662° F.		

The recovery of fat, when the question is merely one of extraction by melting (rendering), is dangerous only if direct fire heat be employed; superheating, ebullition attended by decomposition of the fat, or the formation of inflammable vapours may easily lead to an outbreak of fire.

The danger is, however, diminished, to a certain extent, by the use of steam heat.

The dangerous vapours liberated by tallow and fat must be rendered harmless by conducting them into a fire, where they will be consumed, or by condensation; in the latter event a pressure of 1-2 atmos. (or even higher) may obtain in the vessel; but as the vapours are explosive under these conditions, the pipes and vessels must be fitted with safety-valves.

In raw materials, wherein the fat does not exist *en masse*, but is intimately mixed with the matrix, *e.g.* in the case of bones, hoofs, marrow, seeds, fruits, plants, &c., this simple method of extraction by melting is no longer sufficient; recourse must be had to more powerful means, heavy pressure and solvents. The solvents used for this purpose are often very dangerous in character, chief among them being ether, benzol, and carbon disulphide.

Oil fruits and seeds are first crushed, then heated to 140°, 175°, or even 195°-212° F., and finally subjected to heavy pressure packed in cloths. Owing to the oil-saturated condition of the appliances, oil mills are very risky objects of insurance, and once on fire are difficult to save. The danger of spontaneous ignition of the press cloths and other fibrous materials has also to be taken into account. Nevertheless, no direct danger of fire or explosion is inherent in the process of oil-crushing.

The risks are far greater in works where the fat is extracted with solvents instead of by pressing. In addition to the three dangerous solvents already mentioned, there are others less dangerous, and even harmless: carbon tetrachloride, ammonia, chloroform, benzol soaps, ox-gall; but unfortunately their solvent power is relatively insignificant, and hence they are seldom used in practice, when the extraction of large quantities of fat or oil is in question.

The apparatus used in extracting fat is nowadays of very perfect construction, as indeed is essential in view of the dangerous materials employed; but though they offer a certain guarantee of safety, the claims of absolute security, sometimes preferred by the makers, are not in harmony with truth.

In addition to the usual general requirements laid down in respect of the security of the work and storerooms, the building materials, ventilation, lighting, heating, and the prohibition of smoking, leaky taps, defective pipes, &c., it must be expressly prescribed that *no pressure must be allowed to obtain within the extraction apparatus, even when the solvents are in ebullition*, since any appreciable pressure on the vapour of the solvents increases the explosibility and the danger of a violent explosion.

Another point to be insisted on is that the apparatus must be so arranged that the separation of the raw material, solvent, and fat must be effected in a single train of operations within the apparatus, and without any part of the latter or its appurtenances requiring to be opened, the three main products, fat, spent material, and solvent, being recovered in three separate vessels. Suitable provision must be made for the effective cooling of the vapours given off by the solvent.

With regard to the inevitable waste fat, it should be ascertained whether the necessary care and cleanliness are exercised in this respect. All waste fat must be collected and stored apart, *since all fat in the wrong place means increased danger of fire to the premises*; and even the most

perfect apparatus and greatest precaution will be of no avail if the plant is fouled from top to bottom by fat and fatty waste. Moreover, when any dust is produced on the premises, whether from coal, lignite, sawdust, leather, tan, wool, &c., this dust will gradually accumulate in greasy places, and form a highly inflammable mass, which may be set on fire by the smallest spark or source of heat (steam pipes, &c.). It is possible that numerous fires of problematical origin have been started in this way.

The same care as is bestowed on the raw material is also necessary in recovering and purifying the waste fatty matter, especially since the latter is generally rancid, and therefore in greater danger of fire—especially as regards spontaneous ignition in fibrous materials—than when in a pure state.

Special attention must be directed in fat extraction works to the workmen's clothing, which is mostly very greasy, covered with dust, and may take fire spontaneously if hung up in a warm place or closed cupboard.

## 2. Lubricating Grease and Oil

The mutual contact of machine parts in motion generates heat and warms the parts themselves. This heat is specially great when the speed is excessive or the machine is either very new or very old, and the parts do not fit properly; and the temperature may sometimes attain as much as 550° F., or even more. Similar heating occurs in machines that are overloaded, and therefore exposed to excessive friction, or are fitted with bearings of insufficient length.

Axles and shafts not infrequently get warm (up to 175° F.) in running, but this is not dangerous; and it is also natural that the spindles of spinning frames should grow warm while running at 2000 to 10,000 revolutions per minute. The matter, however, does not end here, but an accumulation and storing up of heat takes place, and it is in this that the danger resides.

To diminish to some extent this accumulation of heat is the object of lubrication, which is not exclusively designed to facilitate the running of the machinery, but also, by reason of the heat-absorbing capacity of the fats and oils, to cool down the machine parts that would otherwise run hot.

In order to perform this dual task, lubricants must possess special properties, corresponding both to the weight and the velocity of the running parts of the machinery. Very fluid lubricants are expelled by centrifugal force in the case of quick-running machinery; if too thick they are squeezed out of the bearings in heavy machines, and if corrosive they attack the metal.

Hence there is no universal lubricant suitable for all kinds of machinery, unless water were employed for this purpose, in which event it would have to be used in large quantity and kept circulating, since it would otherwise get hot too quickly. Water, however, cannot be used in practice as a lubricant; and besides it would rust the machinery; consequently, other means must be sought, capable of producing good results by the use of a small quantity, and of preventing the dangers arising from the heating of the machine parts. These dangers are:—

(a) Ignition of the lubricant, which then burns with a bright flame and may cause damage by fire.

(b) Formation of vapours and gases from the lubricant itself. These vapours and gases are inflammable, and explode when mixed with air. They occur in machines employed for compressing gases and vapours (compressors), and are caused by insufficient cooling of the compressor, excessive volatility of the lubricant, and a lowering of the ignition point of the lubricating oil gases as a result of the high pressure in the compressor. Similar explosions of lubricating oil gases may also take place in engine cylinders.

(c) Ignition of existing combustible gases or clouds of dust, in contact with the hot-running (red hot) axles and machine shafts, thus giving rise to violent dust explosions, not infrequent in flour mills.

In view of these risks, the following requirements are exacted of lubricants:—

1. Sufficient consistence to prevent expulsion, by centrifugal force, in quick-running machinery.

2. For heavy machinery exposed to great friction, the lubricant must not be so consistent as to be liable to be squeezed out.

3. A high flashing and burning point is necessary, to lower the chance of gasification and ignition; a high boiling point is of minor importance in this connection.

4. Flashing should not occur until the oil has been heated to or above 135° C. (275° F.). No lubricant that liberates combustible gases below 110° C. (230° F.) can be classed as safe.

5. When heated to 125° C. (257° F.) and ignited, the lubricant should not continue to burn without a wick.

6. The lubricant should not contain any constituents that can be carried off by the influence of steam.

7. When exposed to high steam pressure and high temperature, lubricants (cylinder oils in particular) should not be gasifiable except with difficulty; and indeed preference should be given to such as cannot be gasified at all, *e.g.* graphite.

8. Lubricants should not lose any of their original properties under the influence of storage, cold, or use.

The importance of the flashing and burning points has been denied in some quarters; but, though this may be true in respect of the former, the burning point undoubtedly plays a very weighty part when a lubricant is required to withstand heat.

Good lubricants do not give off inflammable vapour below 200° C. (392° F.), though in the case of light motors a flashing point of 170° C. (338° F.) may be high enough. The ignition point should range between 280° C. (536° F.) and 340° C. (617° F.); or 220° C. (428° F.) for light motors. The less important boiling point should not fall below 260° C. (500° F.). “Caloricide,” a preventive of heated bearings, flashes at 309°–340° C. (588°–617° F.); a similar preparation, “viscose,” at 350°–380° C. (662°–716° F.).

In addition to the simple lubricants, consisting of fats and oils, there are others compounded from resin oils and adjuncts, such as soap, &c. When these are used, care should be taken to see that they are free from substances like sulphur and acids, that can corrode the metal of the machinery.

Though sulphur attacks metal, a single application of this element (powdered) is sometimes permissible, and indeed advisable, for hot-running axles and shafts, owing to its cooling properties.

Particularly dangerous, by reason of the ease with which they furnish gas and vapour, are the paraffin oils, of which there are a large number. Owing to their poor consistence they are mixed with caoutchouc and lard oil.

Resin oils being cheap are largely used, and form the basis of the manufacture of compound lubricants.

In general it may be said that :—

1. Lubricants of animal origin (tallow, lard, train oil, neatsfoot oil) have the greatest cooling effect on axles and shafts, but render the cleaning rags liable to spontaneous ignition.

2. Lubricants of earthy origin (petroleum, solar oil, Vulcan oil, paraffins) have the smallest cooling effect, but only become a source of danger to the cleaning waste under special circumstances.

3. Lubricants of vegetable origin, and of a non-drying character, stand between the other two kinds in respect of cooling properties; but are the most dangerous of all in imparting fiery tendencies to fibrous materials.

For the extinction of fat fires, see *Fire Extinction*.

Carelessness in the selection and use of lubricants may prove a source of great expense to insurance companies.

Where compressed air is employed, the lubricants used must be of the best possible quality, and fulfil the most stringent requirements, since, under these conditions, the decomposition of the oil is accompanied by the formation of methane, which becomes dangerously explosive in admixture with the compressed air. The high pressure in engine cylinders necessitates the use of a high-flashing oil (minimum temperature 300° C. or 572° F.).

*Flashing and Burning Points of various Fats, Oils, and Lubricants.*

	Flashing Point.	Burning Point (without wick).
	Deg. F.	Deg. F.
Olive oil . . . .	419-500	662
Rape oil . . . .	168-581	662
Cottonseed oil . . . .	338	not a lubricant
Resin oils . . . .	266	329
Poppy oil . . . .	491	662 not a lubricant
Sesame oil . . . .	491	662
Linseed oil (raw) . . . .	600-662	662 not a lubricant
Lard oil . . . .	464	...
Spermaceti oil . . . .	482	...
Compound lubricating oil	500-608	...
Cylinder oil (mineral) . .	466-538	565-633
Shale oil (Scotch) . . . .	266-356	...
Russian Engine oil (dark)	280-320	350-383
" " " (pale)	325-381	448-457

## CHAPTER XXXIX

## RESINS

## 1. General Remarks

RESINS are complex products of vegetable origin, the integral constituents of which are: resin acids, ethereal oils, gums, and a series of supplementary substances, such as cellulose, tannin, benzoic acid, &c. All resins are poor in oxygen, but rich in carbon, and therefore burn with a very smoky flame, requiring a copious supply of atmospheric oxygen to support the combustion.

Resins may be classified as follows:—

Hard resins: amber, benzoin (furnishes benzoic acid), gum lac (furnishing shellac, seed lac), anime, dammar, copal, mastic, olibanum (furnishing incense), sandarach, guaiacum, dragon's blood, aloe, Jalapa.

Soft resins are solutions of resins in the ethereal oils of the originating plants = balsams: turpentine (furnishing oil of turpentine, pine resin, black pitch, colophony, violin resin), copaiba balsam, styrax, and Peruvian balsam.

Gum resins are mixtures of vegetable mucilage, ethereal oils, resins, and gum: asafetida, gamboge, caoutchouc (furnishing rubber), gutta-percha, and balata.

In point of general fire risk, all resins are about equal.

The melting points of resins vary between 107.6° F. (ammoniacum) and 536° F. (amber) (see also *Table of Melting Points*).

When resins are warmed alone or distilled with water, the ethereal oils (oil of turpentine) pass over first, at 212°–320° F. After the elimination of water and the chief bulk of the ethereal oils (which cannot, however, be totally got rid of, even by prolonged dry distillation—see *Colophony*), vapours exhibiting explosive properties make their appearance, and at the same time the resins manifest a tendency to froth over, so that when open fires are used the overflowing mass may easily take fire.

The following resins behave more quietly in boiling: copal, dammar, and colophony; but greater danger of boiling over is experienced with amber, shellac, elemi, sandarach, and mastic, these latter being therefore more risky to work with than other resins.

The gases and vapours liberated on boiling are readily inflammable, and are therefore best conveyed to a gasometer and thence into a furnace fire. As in the case of all illuminating gases, care must be taken to provide fireproof pipes and conduits.

Resin stills must be properly set in masonry, in such a manner that only about one-fourth of the spherical still is exposed to the direct heat of the fire. Careful control of the firing is indispensable.

In melting resin over direct fire, ignition of the vapours and the resin itself may easily occur if the lumps of resin do not uniformly cover the bottom of the pan, but leave vacant spaces that get overheated.

All these dangers, of no inconsiderable magnitude, may be avoided by the use of steam (ordinary or superheated) for heating.

Sometimes, however, it is necessary to first melt the resin over a fire, on account of the contained impurities which must be removed before the resin is fit for further treatment. The ethereal oils have also to be eliminated.

This purification, or that effected by the aid of solvents, must be carried on in fireproof rooms or in the open, away from all naked flame, and isolated from the furnace. The crux of the operation is the point of incipient melting and boiling. No less risky is the operation of purifying by solvents, such as nitrous ether, ether, benzol, alcohol, carbon disulphide, and ethereal oils.

Before accepting the risk of insuring premises where resin purification is carried on, the nature of the solvent employed should be ascertained; and the specially dangerous character of nitrous ether should not be forgotten. With regard to resins in varnish making, see *Varnishes* and *Spirit Varnishes*.

For certain technological purposes resins are required to possess great hardness; and, as the hardest resins are also the dearest, inferior and softer resins are hardened by treating them with metallic oxides (2-20 per cent.): zinc oxide, iron oxide, lead oxides, and manganese oxide, at 365° F. Care is necessary in making these additions, as also in the manufacture of resin soap, since, unless the addition be made gradually, in small quantities at a time, an extremely violent reaction will ensue, very likely to terminate in copious frothing, overflowing, and an outbreak of fire.

The risk may be diminished by adding the resin in a very finely divided condition, as also in the case of soap lyes.

Finely divided resin in the form of floating dust makes a highly explosive mixture with air, and when ignited by contact with flame (see *Colophony*) produces violent dust explosions.

Resins may also become exceedingly dangerous when placed in intimate contact with oxygen, ozone, or carriers of oxygen, these mixtures being capable of spontaneous ignition. Special precautions should be taken to avoid bringing resin or resin dust into contact with ozone, ozonogenic substances, or liquid oxygen.

## 2. Turpentine

Turpentine exudes from coniferous trees either spontaneously or after incision. It consists of solid resin (abietic acid), and ethereal oils (oil of turpentine) constituting 15-30 per cent. of the whole mass.

When turpentine is distilled with water, the oil of turpentine passes over, leaving a vitreous pitch, "boiled turpentine," behind; but dry distillation furnishes colophony in place of this pitch, though oil of turpentine is obtained by this process as well.

Oil (spirit) of turpentine is an ethereal oil. The varieties of oil of turpentine are innumerable, every different country and class of tree furnishing a different product. Hence we can here deal only with generalities. The boiling points range from 302° to 338° F., and the sp. gr. between 0.880 and 0.900. The flashing point is as low as 113° F.

A similar oil (Templin oil) is obtained from pine needles, young twigs, and fresh pine wood by distillation with water; the sp. gr. is 0.880-0.900, and the boiling point 320°-327° F. The needles alone furnish, under the

same treatment, a pine needle oil of sp. gr. 0.875 and boiling point 320° F.

The process of distilling oil of turpentine from crude turpentine is one of peculiar danger, on account of the rapid working necessary to furnish a clear, colourless oil.

Oil of turpentine and its aforesaid analogues exhibit highly dangerous features, being readily combustible, and furnishing vapours that take fire at 95° F. When poured into fuming nitric acid or nitrating liquid (*q.v.*), it takes fire immediately; with iodine it explodes; and when mixed with ether, benzol, and similar dangerous liquids, it may, under certain conditions, set these liquids aflame. The pouring of oil of turpentine into molten resin, asphaltum, sealing-wax, &c., may readily produce ignition should the materials be too hot or in the vicinity of burning fire or naked lights. When oil of turpentine is distilled and only the first distillates are collected, they form a series of readily inflammable and dangerous liquids, boiling as low as 68° F. To this series belongs divinyl, b.p. 68°–86° F.

Exposed to the sun, oil of turpentine absorbs oxygen, or modifies this gas into ozone, of which latter it can take up a large quantity. This ozone is the cause of the above-mentioned ignition of admixed ether, benzol, &c. Oil of turpentine is therefore a carrier of ozone, and in such event exhibits the dangerous properties of this gas (see *Ozone*). Attempts have been made to render oil of turpentine inodorous, but it does not thereby become less dangerous.

An artificial oil of turpentine, *larixolin*, consisting of camphor oil and petroleum, has a flashing point 18° (F.) above that of the natural oil (131° F. instead of 113° F.), and forms a useful substitute for the genuine article. *Paint oil*, another turpentine substitute, is a mixture of petroleum and spirit. *White spirit*, used for adulterating oil of turpentine, is a petroleum distillate passing over at 300°–390° F.; it renders the oil still more inflammable and dangerous.

Oil of turpentine is put to a variety of uses: in the preparation of lacquers, varnishes; as a diluent for thinning down the colours in porcelain painting (and ordinary paint); for bleaching ivory, piano keys, &c.; and as an illuminant in admixture with alcohol.

**Colophony** (violin resin) forms, with oil of turpentine, the principal constituent of crude turpentine. The sp. gr. is 1.070, and the boiling point 194°–212° F., the mass softening at 176° F.

It consists chiefly of abietic acid (m.p. 329° F.) and resin oils, 1–2 per cent. of oil of turpentine being always present.

This presence of oil of turpentine and resin oils stamps colophony as a carrier of oxygen and ozone, and even as liable to spontaneous ignition; for when colophony is finely powdered, the increased surface thus presented leads to a violent oxidation of the resin acids, sometimes so energetic as to cause the powder to take fire by its own heat. On the other hand, lump colophony is not directly dangerous, though readily ignited. The powder should be stored in a fireproof manner, in closed vessels only, and never stocked in large quantities. The great inflammability of the powder is utilised for the preparation of flashing powders (*q.v.*).

The floating dust from colophony powder is very sensitive to flame of every description, sparks, and oxygen or ozone, *i.e.* carriers of oxygen; in this form it is extremely liable to produce dust explosions.

When colophony is subjected to dry distillation it first gives off the volatile constituents, which are recovered at 250°–300° F. in the form of resin spirit or pinolin. These are followed by readily inflammable vapours (from partial decomposition) exploding on admixture with air. The final distillates consist of resin oils.

Colophony is used in soap making, for varnishes, lacquers, sealing-waxes, brewers' pitch (see *Brewing*), for rubbing on violin bows, the preparation of flashlights, and firework charges.

Pinolin, or resin spirit, is highly inflammable, and far more dangerous in respect of fire than either oil of turpentine or resin oil, more particularly when used for application as a waterproofing agent on bricks, tiles, and other products, or when exposed to dry heat in closed vessels or in semi-inclosed places, the vapours then liberated proving a source of very considerable danger.

An artificial commercial pinolin is known, consisting of colophony dissolved in ether, petroleum ether, or benzol, and, by reason of the solvents named, is far more dangerous than the genuine distillate.

**Resin Oils.**—After the passing of the resin spirit in the dry distillation of colophony, two oils distil over (accompanied by combustible gases and vapours of carbon monoxide and benzol), one thick, the other thin. These are the crude resin oils so largely used as lubricants, and furnish, when rectified, an oil of sp. gr. 0.955, boiling at 401° F., at which point it undergoes decomposition.

In point of danger the resin oils are about on a par with petroleum; but, owing to their divergent composition, the risk varies according as they still contain resin spirit or not.

Another form of colophony, identical with the one already described, is furnished when amber is heated.

For hop resin, see *Agricultural Products*.

### 3. Ethereal Oils

The ethereal oils have nothing in common with the fats, except a few physical properties. They are of an oily nature, form grease spots (which, however, disappear on heating), are lighter than water, in which they are insoluble, and are soluble in the same solvents as the fats. Whereas the fats and fatty oils must be regarded as complete chemical compounds, the ethereal oils are mixtures of chemical compounds, partly containing oxygen and partly oxygen-free.

They are organic constituents of various plants, in which they form the source of the characteristic odours; and are partly liquid, partly solid, and then known as camphor.

The following typical ethereal oils may be cited:—

I. Lemon oil, turpentine oil, lavender oil, wormwood oil (vermouth), pine oil, bergamot oil, nutmeg oil, mace oil, eucalyptus oil, juniper oil, and solid camphor. When treated with iodine, these oils detonate with liberation of vapours and great heat.

II. Aniseed oil, fennel oil, camomile oil, rosemary oil, carraway oil, thyme oil, sage oil, and hop oil. These detonate only slightly with iodine.

III. Rose oil, bitter almond oil, clove oil, mustard oil, valerian oil, and amber oil. When mixed with iodine they generate only a moderate amount of heat.

When old, resinified, or rancid, the oils of Classes II. and III. behave with iodine in the same manner as those of Class I.

All the ethereal oils boil at temperatures above 284° F., and decompose at 390°–535° F. They will burn even without a wick, are more easily ignited than fats or oils, and are in general more dangerous than these latter. Exposed to the air, they take up oxygen and then form characteristic carriers of ozone.

A few of the ethereal oils (oil of turpentine) take fire on contact with fuming nitric acid or nitrating liquid.

The direct method of preparing ethereal oils by distilling the plants with water is free from danger; not so when the plants are extracted with alcohol and the resulting extract subjected to distillation (explosion of hot alcoholic vapours).

Outbreaks of fire in these volatile oils, which are prepared and used in large quantities (often 2½ tons at a time), are very dangerous. As in the case of burning fats, water must not be employed for quenching.

#### 4. Camphor

Sp. gr. 0·886. B.p. 399·2° F. Flashing point 125·6° F.

M.p. 347° F. Burning point 140° F.

Camphor is a solid ethereal substance formed from camphor tree oil by oxidation. It is inflammable, burns easily and with a smoky flame, volatilises at 68° F.; is recovered by distilling camphor wood or crude camphor with water, and is purified by sublimation.

The distillation process is free from danger, the amount of heat required being small owing to the ready volatility of the camphor vapours. On the other hand, the purification, by heating to 374°–399° F., is rendered risky on account of the simultaneous formation of explosive hydrocarbon vapours, camphor oil in particular; hence any negligence or overheating during distillation may lead to explosion, which readily culminates in an outbreak of fire. The processes must therefore be carried on in fireproof rooms only, and by the aid of reliable workmen.

When protected from direct ignition, and in storage, pure camphor is free from risk. If allowed to dissipate in the form of vapour and, as is often done as a preventive of vermin, to permeate masses of fibres and textile fabrics, it imparts to the mass (like naphthalene) an increased tendency to maintain glimmering combustion; the vapour itself does not incite spontaneous ignition.

To obtain pure camphor the crude article is treated with benzol, the solution concentrated by distillation to recover the solvent, and the pure camphor separates, in the form of powder, from the cooled residue. This operation is highly dangerous, on account of the benzol and its explosive vapour.

The light distillates passing over at 347° F. in the distillation of camphor form the light camphor oils which, being less dangerous than benzol or oil of turpentine, are used to replace these as solvents for caoutchouc in varnish making, porcelain painting, and the production of lampblack. These light oils flash at about 131° F., *i.e.* higher than oil of turpentine, take fire at 140° F., and boil at 399° F.

The heavy camphor oils distilling over subsequently are still less dangerous, boiling at 536°–572° F.

The most extensive use for camphor at present is in the preparation of celluloid. It is also employed for medicinal purposes and as a protection against moths.

An artificial camphor is prepared by passing hydrochloric acid gas through oil of turpentine. With petroleum, the camphor oils furnish artificial oil of turpentine, or *larixolin* (*q.v.*).

### 5. Caoutchouc (Indiarubber)

Melting point  $257^{\circ}$ – $428^{\circ}$  F.

This gum resin, which though combustible does not burn briskly, furnishes inflammable hydrocarbon vapours and liquid caoutchouc oil when strongly heated.

The process of working caoutchouc is not particularly dangerous, except that temperatures up to  $212^{\circ}$  F. are developed during the operation of mechanically reducing the material between rollers (rubber manufacture).

Caoutchouc is vulcanised and ebonised, *i.e.* treated with sulphur, of which it takes up a large amount, and then furnishes hard rubber, ebonite, vulcanite, and stock for making combs.

Vulcanisation is effected with sulphur at the ordinary temperature, or at  $234^{\circ}$ – $266^{\circ}$  F., or again with the assistance of carbon disulphide, sulphur chloride, or petroleum ether, *i.e.* sulphur solvents; these agents are very dangerous. Certain objections also attach to vulcanising at  $234^{\circ}$ – $266^{\circ}$  F. When vulcanised rubber is exposed to higher temperatures ( $266^{\circ}$ – $302^{\circ}$ – $320^{\circ}$  F.), it takes up more sulphur and assumes a horny character.

Caoutchouc is soluble in benzol (*q.v.*), ether, carbon disulphide, or oil of turpentine; or rather gelatinised, since it merely swells up. This mass is applied to textiles, and when these are dried the solvent is evaporated with formation of explosive vapours. True solutions of caoutchouc may be obtained by using a large proportion of the solvents, or else well rectified oil of turpentine, petroleum, caoutchouc oil, or mixtures of carbon disulphide with absolute alcohol; all these agents are attended with grave risks.

The operation of colouring rubber is attended with risk when the colours are dissolved in benzol or analogous liquids and incorporated with the molten caoutchouc at a temperature of  $257^{\circ}$  F., owing to the possibility of serious outbreaks of fire in the benzol.

Caoutchouc is used for all kinds of articles in general use; also in photography, in the state of a  $1$ – $1\frac{1}{2}$  per cent. solution in benzol. The waterproofing of articles of clothing, mantles, textiles, curtains, &c., with dissolved caoutchouc is a very risky process, owing to the solvents; and the waterproofed articles acquire a higher tendency to take fire than they already possessed.

There are numerous caoutchouc substitutes, chief among them being the artificial indiarubbers (factice) prepared from—

(a) Oils (colza oil, castor oil) and sulphur chloride (b.p.  $280\frac{1}{2}^{\circ}$  F.);

(b) Oils with about 15 per cent. of sulphur, the whole heated to  $482^{\circ}$  F.

In either case, such large volumes of insupportable vapours are disengaged that the operation can only be performed out of doors. The

processes are not in themselves very objectionable, though precautionary measures are highly necessary on account of the highly heated oil.

Guttapercha, which is also obtained from tree sap, is so similar to caoutchouc in point of fire risk, that what has been said of the one may equally apply to the other.

The recovery, or devulcanising, of pure rubber from worn-out rubber articles and waste is a continually growing practice. The process is free from risk so long as no dangerous solvents are used, but only innocuous means, such as moderate warmth, water, lime, alkalis, ammonia, or glycerin. As, however, use is also made of dangerous agents like warmed naphthalene, readily inflammable ether, and alcohol, it is necessary that these substances should be specified when the risk of such factories is to be estimated.

## CHAPTER XL

### VARNISHES AND LACQUERS (Spirit Varnishes)

#### 1. Varnish Making

THOUGH many insurance companies will not accept the risk of varnish works, it is necessary to devote some consideration to these establishments, partly because they may occupy contiguous sites to insured premises, and partly because varnish making is sometimes carried on as a branch business, and both varnishes and lacquers are largely used. Hence, and in view of their unusually dangerous character, a knowledge of the manufacturing processes cannot be other than useful.

It must be mentioned at the outset that the nomenclature of the individual products is often extremely arbitrary, one and the same article being known by various names.

By the term varnish or lacquer is understood an oleaginous or resinous (or even oleoresinous) liquid which is applied as a protective coating to many articles, to prevent the penetration of moisture, air, vapour, or smoke, or else to impart a lustrous, smooth, or even dull appearance.

Varnishes may be divided into the following classes:

1. Oil varnish, usually boiled linseed oil, more rarely poppy or nut oil.

2. Lacquer varnish (true lacquer, also called spirit varnish). This class consists of resins dissolved in alcohol, wood spirit, acetone, benzol, or petroleum ether; or collodion wool dissolved in amyl acetate.

3. Oil lacquer varnish: solutions of resins in linseed oil, oftentimes thinned with oil of turpentine or benzol; hence a mixture of 1 and 2.

4. Turpentine lacquer varnish: solutions of resins in oil of turpentine.

5. Resin oil lacquer varnish: solutions of resins in resin oils.

There are also sundry special lacquers, such as dull lacquer (sandarach in ether, benzol, or toluol), zapon lacquer (collodion wool or celluloid in amyl acetate), asphaltum lacquer (asphaltum in oil of turpentine).

The resins most in use for lacquers and oil varnishes are, copal, dammar, anine, sandarach, mastic, shellac, pine resin, colophony, amber, and asphaltum.

The boiling of oil and spirit varnishes is one of the most dangerous of all industries. Oils (chiefly linseed) have to be boiled at temperatures from 250° to 750° F., explosive vapours being formed and the oils rendered highly inflammable, or even liable to take fire spontaneously. The resins have to be heated to 250° F., and melted at temperatures up to 680° F., an operation also attended by the liberation of explosive vapours. Finally, pressure up to 5 atmos. must be employed.

The oil varnishes are prepared in several different ways:

1. By boiling linseed oil at 250°–465° F. in fixed or movable pans over an open fire;
2. By boiling the oil with steam in jacketed open pans, at 270° F. =  $4\frac{1}{2}$ –5 atmos. pressure, and then beating the oil into fine drops with paddles to facilitate the action of the air;
3. By boiling the oil in closed vessels fitted with flues, and then blowing hot air through the liquid; or, finally, by
4. Boiling with steam superheated to 750° F.

Of all these, the first is the most dangerous, on account of the difficulty of regulating open fires.

The following points of danger are present in all four processes: linseed oil, even before the boiling point is reached, liberates (at 300°–660° F.) explosive and spontaneously ignited vapours; it easily boils over, especially when impure; the rise in temperature is very irregular, difficult to control with an open fire, and often jumps up suddenly, especially at higher degrees, whereupon dangerous overflowing readily ensues; finally, the oil, or the added material, readily burns on to the walls of the pan, bakes hard, and helps the pan bottom to grow red-hot, which easily leads to an explosion.

The melting of the resin, and the mixing of this and other added ingredients with the hot oil, are accompanied by the formation and liberation of inflammable vapours.

Where collodion wool and even guncotton are employed with preparation of zapon lacquer, the danger is equal to that incurred with blasting explosives.

The precautionary measures to be adopted against these risks can only ameliorate, and not entirely obviate, them. They are as follows:—

The rooms, building materials, lighting, heating, firing, ventilation, and the prohibition of smoking or the admittance of unauthorised persons, must fulfil all the usual requirements laid down in respect of other highly dangerous materials and premises. The special regulations include: prohibition of the filling of boiling pans up to more than two-thirds of their capacity; provision of overflow channels and vapour flues, as well as of well-fitting lids (even to portable pans) that can be closed immediately in the event of the contents taking fire; the furnaces must be fed from outside only, and under the charge of a reliable stoker; the liberated inflammable vapour must be either condensed in a proper manner, or else led away into the open, to a point remote from danger. Owing to the possibility of the flame lighting back to the pans, the practice of conducting these vapours into the furnace fire and consuming them there is not free from objection, and should only be permitted

when the arrangements are unimpeachable and an appliance is provided for reliably preventing any lighting back, the pipe being, above everything, fitted with fine wire gauze where it debouches under the grate. Cold oil vapours are no longer explosive, only such as are hot.

The fireplaces must be so arranged that, when the pans are charged with oil and added materials to the specified limit, the contents are at least  $3\frac{1}{2}$  inches higher than any point touched by the flame.

Resin should be melted in a separate room, all the foregoing precautions being observed. The mixing of the oil with the adjuncts must be effected away from any open fire, and only when both ingredients are cold.

All temperatures must be accurately controlled with suitable, fixed thermometers.

No other substances may be stored in rooms used for the boiling of oil, melting resin, and mixing. A sufficient quantity of sand, earth, or ashes must be kept close at hand for extinguishing any outbreak of fire; good service in this respect may be done by bags or other coverings, preferably impregnated. All extinguishing agents must be protected from frost during the winter.

Burning varnish or lacquer must never be extinguished with water, only the above mentioned substances being capable of doing this work.

Linseed oil becomes varnish when it has taken up a certain amount of oxygen, of which gas it is able to absorb and fix up to 30 per cent. of its own weight. This absorption occurs not only during the boiling process, but also, and to a still greater extent, afterwards, when exposed to the air. Since the fixation of oxygen is a slow process, attempts have been made to accelerate it by boiling the oil with substances rich in oxygen, *e.g.* manganese dioxide, manganese borate, litharge, and minium, all carriers of oxygen, or by blowing air into the oil. With these adjuncts the oxidation process can be completed within 20 hours, whereas otherwise it takes several days.

Should the oil be imperfectly oxidised, owing to lack of time or an insufficiency of oxidising agents, and the defective varnish be used for coating, &c., porous, fibrous articles like textiles, feathers, paper, mill-board, artificial flowers, &c., the process of oxidation will continue, a considerable amount of heat being formed. So long as this heat can dissipate into the air danger is less imminent, though not entirely absent; it will, however, become so if the articles be kept, stored, or packed in such a manner that the heat is prevented from escaping. Under these circumstances the retained heat will produce charring, and, finally, the spontaneous ignition of the articles in question, the case being analogous to that of oily rags. In some articles this danger is considerably augmented by the practice of dusting them over with wool dust or similar powders.

Oil varnish also presents certain dangerous features when it comes to be used, being both ignitable and explosive, even spontaneously so, the risk being increased by the difficulty of ascertaining in practice whether it is really saturated with oxygen or not. In the former event the danger of spontaneous ignition is non-existent.

The drying and hardening of a coat of varnish is not such a simple operation as the drying of substances merely wetted with water, but constitutes a stage in the actual formation of the varnish itself, which is

not complete and free from danger until the coating has dried quite hard. Before this condition is attained there are still three phases to be traversed: (1) the volatilisation of the solvent (oil of turpentine, benzol, ether, alcohol, oil vapours, &c.), which is inflammable, and forms explosive mixtures with air—this operation is complete in 4–6 hours in the case of good varnish, thoroughly saturated with oxygen; (2) the drying of the coating, for which 12–14 hours are necessary; (3) the hardening of the mass, this taking 8–12 hours.

In the case of unsaturated varnish the total duration of the process (22–42 hours) is increased four- or fivefold; and the occurrence of such delay is an indication that the varnish is unsaturated and may fall a prey to spontaneous ignition.

An important, and at the same time dangerous, appliance in connection with the use of oil varnish is the lacquering stove, in which the lacquered articles are dried and finished. The temperature in these stoves ranges from 120° to 160° F., and since the formation of explosive mixtures of vapour may occur, they must be fitted with proper ventilating outlets discharging into flues out of all communication with fire. Efficient ventilation must be provided in the room where the stove is located; naked lights must be prohibited, and the stove must be kept in good condition and the brickwork free from leaks through which any inflammable vapours could escape. Lacquering stoves are sometimes heated with hot air of high tension. Explosions in these stoves, which are charged with inflammable vapours, may readily happen, and therefore all fire or sparks should be rigidly excluded. The danger may be diminished by the introduction of carbon dioxide into the air of the stove, 10 per cent. being sufficient, though even in this event no guarantee of safety is possible.

The dangers of varnishes and lacquers increase in proportion to the dangerous character of the solvents used, the benzol and ether varnishes being the worst in this respect. Of late the extremely dangerous nitrous ether (b.p. 62° F.) has been largely used, but should not be employed except when greatly diluted with alcohol.

Recent substitutes for the ordinary lacquers and varnishes consist of less dangerous mixtures of nitrocellulose or celluloid with dichlorhydrin and epichlorhydrin, both of which latter substances may be employed for dissolving resins, thus dispensing with the risky operation of melting the resin over an open fire.

The oily wadding and fibrous material from varnish filters are extremely liable to spontaneous ignition. Experiments have shown that these waste materials can attain an internal temperature of 280 $\frac{1}{4}$ ° in 15 minutes, rising to 480°–570° F. and over in 45 minutes. They char rapidly, and burst into flame when opened out; hence they should be removed daily and preferably burned in the boiler fire.

The adjuncts (so-called driers) used to hasten the drying of varnish also form spontaneously ignitable substances when dissolved in and combined with the oil. Of these products, the so-called oleates and linolates, special mention must be made of manganese linolate, which is particularly prone to spontaneous ignition whilst in the freshly precipitated, warm condition. Special attention should therefore be directed to these products where formed in any quantity.

Heat-resisting lacquer varnishes have been prepared that are able to

stand dry heat up to 930° F. and moist heat up to 480° F. These form an excellent anti-inflammable protective coating for the articles to which they are applied, but their preparation is a dangerous process. The residue left after distilling fatty acids at 570° F. is mixed with litharge and minium, and treated with superheated steam at 750°–1110° F. for 6 hours. After cooling down to 392° F. the vapour of petroleum is passed through the mass; and when quite cool, the product is thinned down into a workable consistency with crude benzol. The entire process is dangerous, both on account of the materials and the high temperatures employed, as also by reason of the liberation of benzol vapour during the application of the varnish. On the other hand, the varnish is harmless and dry, and forms a good protective agent for readily inflammable articles.

## 2. Linoleum, Oilcloth

The manufacture of linoleum and similar products necessitates the use of a thorough normal oil varnish that has been completely oxidised (*e.g.* containing about 27 per cent. of oxygen). For this purpose the oil is repeatedly allowed to fall in the form of rain at a temperature of 130° F., until it has become quite viscid, and is then dried at 104° F. until spongy. Higher temperatures being unnecessary the process is less open to objection than those we have just been discussing.

On the other hand, the grinding of the cork dust or meal required for making linoleum is not exempt from the risk of explosions, which may even occur spontaneously. This dust ignites on contact with flame or sparks when floating in the air, and, like greasy rags, is liable to spontaneous ignition when contaminated with oil. Lumps of metal, stone, or other hard articles in the cork may produce sparks in the mill.

Care must be taken to clear away all cork dust deposited on hot pipes or vessels; to keep such dust away from all places where fatty matters, wax, paraffin, or resin are being treated; to burn all oily cork dust, and otherwise deal with the same as is done with greasy rags.

In linoleum factories use is also made of dangerous solvents (petroleum ether, benzol, carbon disulphide; sometimes in conjunction with heat). Again, the passing of the product through hot rollers is not free from risk, though, on the other hand, the finished article is comparatively safe.

Greater danger attaches to works where oilcloth is made, since here, in addition to the use and volatilisation of very dangerous solvents, there is the risk of electrical excitation, which may lead to the ignition of the vapours. Even the first process of all, painting the fabric with linseed oil, varnish, resin solutions, lampblack, and oil paints, sometimes give rise to spontaneous ignition. The drying process, which is accelerated by the addition of carriers of oxygen (*q.v.*), and the rolling of the finished cloth with steam-heated rollers, also present a series of risks.

A very important operation is the final drying, which is effected in special rooms, at a temperature of 100°–140° F., sometimes heated with waste furnace gases. The atmosphere of these rooms is in the highest degree explosive, and the slightest spark from the heating pipes may have disastrous results. Hence such rooms must be perfectly fireproof in every respect, especially as regards construction; and the vapours

must be conducted to a safe place by means of efficient ventilating appliances.

In addition to these dangers comes the risk of electrical excitation, produced by the friction of the resinous cloths during rolling and drying, and, in the opinion of some, also by the friction of the currents of drying air on the cloth. So great is this excitation that sparks more than an inch in length can be drawn out of the hanging cloths, a highly objectionable phenomenon in an atmosphere laden with explosive vapour (see *Benzol and Electricity*).

Happily, this danger can be obviated by humidifying the air of the rooms, especially in dry weather. This humidification must extend both to the air of the room (by the aid of waste steam) and to the flooring (by sprinkling), and must amount to at least 70 per cent. of relative moisture (see *Benzol*). The employment of an efficient hygrometer (*e.g.* that of Koppe) should be made compulsory in all places where humidification is practised as a preventive of danger.

## CHAPTER XLI

### WAXES

WAXES may be of animal, vegetable, or mineral origin :—

Animal waxes: beeswax and spermaceti.

Vegetable „ palm wax (carnauba, ceara wax).

Mineral „ ozokerite (*q.v.*) ceresin.

Those of the two former classes melt below the boiling point of water (122°–194° F.), burn with a luminous flame, boil at about 480° F., and then first liberate inflammable vapours, but in far smaller amounts than the resins and fats. Hence they are less dangerous than these bodies.

Of the two animal waxes, beeswax is less dangerous than spermaceti. On the other hand, the mineral waxes are about on the same plane of risk as the resins and fats, since they yield inflammable vapours at temperatures far below their boiling point (see *Ozokerite*).

For the technical treatment of waxes use is often made of the dangerous solvents ether, carbon disulphide, benzol, petroleum spirit, &c. The ethereal oils and chloroform are safer, but being too dear are seldom used.

The danger of the waxes is often increased by the practice of melting them with 5–10 per cent. of fat or tallow to facilitate the after treatment. Larger additions of paraffin, ceresin, or resin are also given, and correspondingly augment the risk. Adulterated waxes are in greater danger of fire than the pure article.

The numerous polishes and similar preparations of wax now in technical and domestic use are usually more dangerous than the waxes themselves, owing to the presence of added alcohol, oil of turpentine, and other inflammable substances. These preparations are liable to set hard, and it is then a common practice to warm them over an open fire; a very risky operation owing to the impossibility of controlling the tem-

perature, as numerous accidents have demonstrated, especially in the case of beeswax (floor polish).

Burning wax and wax preparations must not be quenched with water, since that liquid merely carries away the floating molten wax and thus spreads the flame; for this purpose, sand, earth, ashes, or cutting off the air supply form the best extinguishers.

Melting point of various waxes: beeswax,  $142^{\circ}$ – $158^{\circ}$  F.; Japan<sup>r</sup>wax,  $125^{\circ}$ – $137^{\circ}$  F.; palm wax,  $161\frac{1}{2}^{\circ}$  F.; spermaceti,  $122^{\circ}$ – $129^{\circ}$  F.; Chinese insect wax,  $179\frac{1}{2}^{\circ}$  F.

## PART VIII—DANGERS FROM PETROLEUM, MINERAL OILS, TAR, ETC.

STRICTLY speaking, the term “mineral oil” signifies the product furnished by the dry distillation of coal, lignite, wood, peat, shale, bituminous rock, ozokerite, or asphaltum, whereas “petroleum” implies the natural (crude petroleum) oil issuing from the earth in association with gaseous liquid and solid matters. Hence petroleum is really nothing but a mixture of numerous natural mineral oils, *i.e.* a natural product, whereas the mineral oils are manufactured products, prepared by the distillation of the tars in which their constituents are contained.

It is difficult to give a lucid summary of these substances, the names of which are frequently bestowed at random. The mineral oils obtained from tar will be detailed under that heading; and for the oils derived from petroleum, ozokerite, asphaltum, and bituminous substances, the following short list will suffice for our purpose:—

Petroleum (crude) furnishes the following products:

	Popular Name.
Petroleum ether (keroselene, rhigolene).	
Gasoline (canadol).	
Benzine (naphtha).	
Ligroin.	Benzine.
Cleaning oil (petroleum spirit, artificial turpentine).	
Illuminating oil (petroleum, rock oil, Kaiser oil).	Burning oil.
Paraffin oil (Vulcan oil, Phœnix oil).	Lubricating oil.
Paraffin.	Paraffin.

Ozokerite (mineral wax) furnishes:

Photogene.  
Paraffin.  
Ozokerite.  
Ceresin.

Asphalt (asphalt rock, bituminous shale) furnishes:

Volatile oils.  
Lamp oils.  
Asphaltum (mountain pitch, Syrian bitumen).

## CHAPTER XLII

### CRUDE PETROLEUM

In respect of fire risk, the crude petroleum are less uniform in character than the fats and oils, the risks of which are confined within narrow limits, while those of petroleum have a wide range. Many of them contain gases that are liberated at the ordinary temperature, and, when condensed to the liquid condition, boil a little above the freezing point of water. Such gases do not occur in fats or oils. Other constituents of crude petroleum are extremely volatile and inflammable, the vapours forming explosive mixtures with air. Finally, other constituents are solid, are not easily ignited, and do not explode until high temperatures are attained.

The low-boiling and highly volatile constituents of petroleum and mineral oils belong to the most dangerous of substances so far as risk of fire and explosion are concerned. However, as the boiling point rises and the volatility diminishes, the danger also lessens, until we arrive at the paraffins, which are about on a par with the fats and oils.

The serial order of the various constituents of petroleum, classified in accordance with their boiling point and volatility (fire risk), is about as follows :—

Boiling Point.	
Gaseous oils . . .	34°–167° F. }
Benzine . . .	167°–302° F. }
Petroleum . . .	302°–518° F. }
Solar oils . . .	518°–572° F. }
Lubricating oils	} 572°–752° F. }
Paraffins . . .	

more dangerous than fats and oils.

the same general fire risks as fats and oils.

In one particular the mineral oils exhibit a far smaller risk than the fats and oils, namely, in connection with the spontaneous inflammability of fibres (*q.v.*). An attempt to draw an approximate comparison between petroleum oils and other dangerous liquids has been made in the following table, those of equivalent fire and explosion risk being placed in juxtaposition :—

Mineral Oils.	Other Substances.
Gaseous mineral oils.	Vapours of ether, carbon disulphide.
Petroleum ether, gasoline, ligroin.	Hot ether and carbon disulphide.
Benzol, benzine, wood spirit.	Cold       "       "       "
Petroleum (flashing at 70° F.).	Hot alcohol (96–99 per cent.).
Kaiser oil, Solar oil, photogene,	Cold       "       "       "
tar oil.	Fats and oils.
Paraffin, naphthalene.	Lubricating greases, resins.
Pitch and residual resins.	

It will be readily understood that these proportional risks will undergo considerable modification under the influence of even slight

changes in the constitution of the mineral oils, a condition to which, moreover, they are peculiarly liable.

The recovery of mineral oils from crude petroleum, &c., is effected by fractional distillation, *i.e.* distillation accompanied by separate collection of the distillates at certain temperatures.

The operation, which is conducted over an open fire and at temperatures extending up to 750° F., is one of considerable danger, if only on account of the large quantities (25–30 tons) treated at a time. The same applies to the refining of certain mineral oils with sulphuric acid, for separating the empyreumatic resins and oils, the ammonia and free carbon, by reason of the accompanying liberation of inflammable gases (sulphuretted hydrogen and hydrogen) and heat.

Since mineral oils readily boil over when heated in closed vessels, the stills should not be filled to more than two-thirds of their total capacity (in exceptional cases to four-fifths). This last-named limit must not be exceeded, even when working on the small scale, the oils increasing in volume by one-tenth when heated.

The cooling of the distilled vapours must be very thorough, and, in view of the large amounts of material treated, entails the use of considerable quantities of water. By this means the vapours must be cooled down to 175° F. at least before exposure to the air, since, otherwise, spontaneous ignition of the strongly heated vapours will be imminent.

Mineral oil refineries should be well protected from lightning by a perfect system of lightning conductors, which must be examined every spring.

The sole means of remedying outbreaks of fire is by isolating the various portions of the plant: stills, filling sheds, barrel stores, reservoirs, and other buildings. This is particularly necessary in the case of storage tanks, which often contain very large quantities of oil; the best method of securing such isolation is to surround them with a wall of earth, extending all round without interruption and enclosing so large a space that no overflowing of oil from burst tanks will be possible.

The tank covers must be supported on fireproof pillars (covered with flameproof material in the case of iron). They must be of flat shape and arranged for the accommodation of water, to cool the contents of the tanks in hot weather, and prevent or diminish the liberation and escape of oil gases and vapours under the influence of the sun's rays. The covers should be provided with flues, capped with wire gauze, to prevent the dangerous accumulation of gases and vapours.

In large establishments all vessels containing oil should be kept open in such a manner as to prevent any dangerous pressure in the event of an accumulation of vapour, such as may easily occur in hot weather.

According to Intschik, the volatility of the lighter constituents of petroleum is so great, that a loss of  $1\frac{1}{2}$  per cent. from this cause is sustained in Baku during the summer months. The remedy he proposes, namely, storage in tightly closed tanks, cannot be recommended, by reason of the increased danger of fire and explosion with which it would be attended. The loss of volatile constituents could be diminished by cooling, since at low temperatures the liberation of gas greatly declines; whereas the use of hermetically sealed covers would be dangerous in the absence of efficient cooling appliances.

As shown by Intschik, the loss of various mineral oil constituents by

evaporation is very considerable. Taking the case of crude benzine as an instance, the losses sustained by evaporation amount to:—

In the Open at 32° F.	In the Refinery at 44½° F.	In the Laboratory at 68° F.
During the		
1st hour . . 12 per cent.	15.6 per cent.	24.3 per cent.
2nd „ . . 33 „	33.0 „	35.0 „
3rd „ . . 33 „	34.0 „	37.0 „

However desirable the ventilation of full oil tanks may be, it is at least equally so in the case of tanks that have been emptied, but still contain small residual quantities of oil, owing to the tendency of these traces of oil to give up their volatile constituents to the air of the tank, which thereby acquires explosive properties. This tank air is very dangerous, as was shown in the case of an accident that happened at Berlin in 1885, where an empty oil tank, that had been shut up for two months, caused an outbreak of fire on being inspected with an open light. All open fires, lights, &c., must be kept at least 200 feet away from such installations.

Considerable risk attends the distillation of crude petroleum, particularly at the commencement of the process, since it is at this stage that the dangerous gaseous products pass over.

Serial order of distillates (the figures in brackets indicate boiling-points):—

At 40° C. (104° F.): Ethane (−19° C.), propane (−37° C.), methane (−164° C.), ethylene (−105° C.), butane (1° C.), butylene (3° C.), propylene (−18° C.). These are gaseous products.

At 104°–158° F.: Petroleum ether, pentane, keroselene, rhigolene,

At 158°–194° F.: Gasoline (Canadol),

At 176°–212° F.: Petroleum benzine (naphtha),

At 194°–248° F.: Ligroin,

At 248°–302° F.: Cleaning oils,

At 302°–518° F.: Petroleum (termed Kerosene I. in Russia).

At 518°–572° F.: Solar oils (termed Kerosene II. in Russia), Kaiser oil, water-white.

At 572°–752° F.: Lubricating oils, paraffins.

The last named is usually distilled with superheated steam.

The order of risk is as follows, the most dangerous coming first:—

1. The gaseous products.
2. Petroleum ether.
3. Gasoline.
4. Benzine.
5. Ligroin.

6. Cleaning oils.
7. Petroleum.
8. Kaiser oil, water-white.
9. Solar oil.
10. Lubricating oils, paraffins.

Numbers 2, 3, 4, and 5 are characterised by excessive volatility, inflammability, and proneness to form explosive mixtures with air. These are the oils that, when the gaseous products have escaped, constitute tank air and the source of loss during storage.

When mixed with air and burned in suitable appliances they furnish a very bright flame (see *Air Gas*) that is much used for illumination

purposes in yards, circuses, halls, &c.; when they burn under pressure, the danger is by no means small (see *Lighting*).

The boiling points of these oils are subject to fluctuation, the average being :—

Petroleum ether . . . 113° F.	Petroleum benzine . . . 194° F.
Gasoline . . . 122° F.	Ligroin . . . 248° F.

They can be used wherever benzol finds employment, their properties being similar, but of course the risk is thereby increased.

It may also be mentioned that the names of these oils are bestowed in a very arbitrary manner, the term ligroin being applied in one oil district to the product that in another is called benzine or gasoline. Each of the chief producing centres: America, Baku, Galicia, Roumania, Alsace, has its special nomenclature, determined by differences in the constitution of the oil.

Under any circumstances, the whole of these products must be regarded as dangerous substances, and all alike as concerns fire and explosion risk; since, though it may be assumed that ligroin is less dangerous than petroleum benzine, it is not always possible to assert that the oil in question is really ligroin. The practice of mixing these different grades together, in accordance with market conditions, is frequently adopted, and can only be detected by chemical examination.

Benzine is also sold as "hydririne" (see *Air Gas*).

These oils are very extensively used, more particularly for lighting purposes, and carburetting gas of low illuminating power (especially water gas).

The most important product furnished by crude petroleum is noticed in the next chapter.

## CHAPTER XLIII

### PETROLEUM (Kerosene)

Sp. gr. 0.780–0.820. B.p. 302° F. Flashing point 70° F. or 118° F.

THE more highly refined varieties are: Kaiser oil, water-white, Solar oil, photogene, which mostly flash at 107°–118° F. Proper lamp oil is not, of itself, explosive, nor is it ignited when a burning match is plunged into the liquid; in fact, with good oil the match should go out under these conditions. This low tendency to ignition is caused by lack of oxygen, of which element petroleum contains very little, in some cases none at all.

The oil, however, will very quickly ignite, on the application of a match, when it has been warmed to 85°–95° F., even a glowing match being then sufficient to set it alight (see *Lighting*).

Lamp oil becomes explosive when re-mixed with gaseous or volatile constituents of crude petroleum, a circumstance apparently by no means uncommon. The liberated vapours then form with the air above the oil

an explosive mixture which produces lamp explosions when the oil in the latter attains 85°–95° F., as it easily may do from the heat of the lamp flame or of the room. Petroleum is also rendered explosive by additions of alcohol or ether, even in proportions of about 10–15 per cent.

Violent shaking, which causes a liberation of the more volatile substances, may also give rise to lamp explosions, especially when the lamp is knocked about or let fall.

All attempts to free liquid petroleum from its dangerous properties have proved unavailing; and this is very natural, seeing that it is the vapours, and not the oil itself, that cause the danger. The means employed, however, have no influence on these vapours, and even though they carry off the latter in volatilising, do not diminish their liability to explode.

True, some of the agents used for the above purpose, *e.g.* petrolith (camphor, common salt, and soda) may improve the lighting power of the oil, but this result must not be regarded as reducing the explosive tendencies of the oil vapours.

With a view to minimising the risks of petroleum, and at the same time reducing the expense of barrels and freight, attempts have been made to convert it into a safe solid form, with more success, be it said, than the endeavours referred to above. With this object, the oil is heated with resin- and wool-fat soaps, stearin, paraffin, or fatty acid mixtures; but, as the temperature must be raised to 300°–380° F., the operation is not free from danger, explosive vapours being formed.

In order that the solidified oil may fulfil expectations, and be really safer during storage and transport, besides saving the cost of barrels, the solidification must be very complete and comply with the following requirements:—

1. The solidified oil must not exhibit any drip of liquid constituents.
2. The mass must not liquefy or part with any liquid constituent when heated to 112° F.
3. It must keep for a definite period in the solid state.

These requirements, however, have not been completely fulfilled by any of the petroleum preparations hitherto introduced, and consequently, in the absence of proper coöperation, they are more dangerous than the liquid oil that is packed in secure barrels.

The yellowish-brown petroleum briquettes, weighing about 8 lbs. apiece, used for steam raising, are prepared by the partial saponification of petroleum or residuum. Owing to their low melting point (175° F.) they cannot very well be used alone, as they would run down through the fire-bars. They have therefore to be mixed with coal. At 122° F. they give off combustible vapours, and even the small pressure caused by their own weight is sufficient to cause the oil to exude. Hence they do not fulfil the requirements laid down in respect of good solidified oil (see *Ozonal*), and are by no means free from risk.

The solidification of petroleum being an important matter to many industries, the attainment of this end will undoubtedly be secured; at present the existing kinds of solidified oil must be regarded with some suspicion, more especially in so far as their keeping properties are concerned.

Large stores of *empty* petroleum barrels are always looked upon as dangerous; but, though it must be admitted that an outbreak of fire in

such a store may attain serious dimensions, the danger of fire should not be overestimated. Empty barrels are not likely to initiate an outbreak of fire, provided they are properly stored, *i.e.* when they have been completely drained of oil, the tap- and bungholes being left open and turned downwards while the barrels are drained, the floor of the store being sloped so that the drainings can run away to a sheltered spot.

When the oil is one flashing at or above 70° F., such stores of empty barrels are not a bit more dangerous in respect of fire than equally extensive stores of timber or wooden articles. On the other hand, barrels that have held crude oil, or petroleum containing very volatile or gaseous constituents, are far more dangerous, and the risk will be on a par with those of the stores in oil refineries. A similar difference in the degree of danger has been observed on Russian river steamers; so long as petroleum residue (masut) flashing at 158° F. was used for raising steam outbreaks of fire were rare, but became frequent when a masut of lower flashing point (116° F.) was introduced.

Experiment has also shown that the wood of petroleum barrels is not permeated to any extent with oil, owing to the protective action of the glue lining employed; and that a candle flame has no more effect on this wood than on that of any other kind of barrel. Oil barrels that have been opened and drained in a proper manner, then stored for some time, and afterwards tested by heating them in an open fire and inserting a naked light through the bunghole, proved quite free from explosion risk.

Similarly, in connection with other methods of application, it may be said that petroleum is not an invariably dangerous substance. When properly refined, it may be safely used for a number of purposes, provided it be kept cool; but when impure it is always risky.

Great objection attaches to its employment as a remedy for boiler fur while the boiler is still hot, since under these conditions the oil becomes heated, and gives off vapours, which may ignite and explode on contact with the flame of the lamp necessarily carried by the man working inside the dark boiler. In fact, several very violent boiler explosions have been traced to this cause (see *Boiler Fur*).

Ozonal is a petroleum solidified with the aid of resin soap, and is used for laundry purposes in the form of yellowish-brown, gelatinous cakes. It takes fire immediately on contact with flame, being highly inflammable. Nothing further can be said in respect of its fitness to rank as a solid petroleum.

The use of petroleum, especially the heavier oils, in agriculture as a preservative for liquid manure is not dangerous, unless the oil contains volatile constituents that may be set on fire by a dropped match or an overturned lantern.

The question of raising the flashing point of petroleum oil from the present level of 70° F. has been widely discussed. It has been demonstrated that this flashing point is not high enough to prevent accidents from fire, and that the sole preventive is the use of safe oil (water-white, Kaiser oil). To save increasing the cost of oil by raising the flashing point it has been proposed to legislate on the question of lamps, and to prescribe the adoption of certain forms of lamps for burning oil. It has already been stated, in the section of *Lighting*, that such a course would not suffice to prevent explosions, since many oil fires are due to

other causes than lamp explosions. Even the most perfect type of lamp would not be exempt from the risks incurred in filling or on overturning the lamp itself, in conveying and carrying the oil, in lighting fires with petroleum, or throwing oil on the fire.

It is technically impracticable to enforce the use of a standard lamp in daily life, but far easier to insist on a higher flashing point for lamp oil, and forbid the sale of any that flashed below  $90^{\circ}$ – $96^{\circ}$  F.

Of the other mineral oils, though not possessing the character of oils or fats, mention may be made of benzol and toluol.

## CHAPTER XLIV

### BENZOL

BENZOL, benzene, benzine oil, Benzinum lithanthracium, coal-tar naphtha. Sp. gr. 0.884. Vapour density 2.770. B.p.  $177^{\circ}$  F. (of 90 per cent. benzol  $179\frac{1}{2}^{\circ}$  F., and 50 per cent. benzol  $190\frac{1}{2}^{\circ}$  F. Flashing and ignition point zero F. (the 90 per cent. article at  $2^{\circ}$  F.). Solidification point  $32^{\circ}$  F. M.p.  $41^{\circ}$  F.

In the following lines the wider term "benzine" will be employed, because, as a matter of fact, benzine is more largely used for industrial purposes than the chemically purer benzol, which is difficult to prepare and really unessential for the majority of industrial uses.

Formerly the name benzine was confined to coal-tar benzol, but now three kinds are known, all exhibiting analogous physical properties and risks, though differing considerably in chemical behaviour, &c.

- (1) Coal-tar benzol (benzine), from coal-tar.
- (2) Lignite benzine, from lignite tar.
- (3) Petroleum benzine, from mineral oil.

The chief chemical difference between them consists in the fact that coal-tar benzol can be nitrated into nitrobenzol, which is used in aniline manufacture, whereas the other two kinds cannot be employed in this way.

There are three commercial grades of coal-tar benzol:

- (1) The almost chemically pure benzol, b.p.  $176^{\circ}$ – $180^{\circ}$  F.
- (2) A mixture of benzol and toluol, b.p.  $176^{\circ}$ – $248^{\circ}$  F.
- (3) Benzoline (grease eradicator), b.p.  $248^{\circ}$ – $338^{\circ}$  F.

The latter is safer than the other two, and is very rarely the cause of fires, though largely used as a detergent in numerous households.

The value of benzine depends on its percentage content of distillate passing over at  $212^{\circ}$  F. According to the result of this test the benzine is classed as 99, 93, 80 per cent., and so on.

Benzine is frequently mixed with the more volatile oils and ethers from petroleum and tar; as the risk is thereby augmented, too much reliance must not be placed on the so-called industrial benzenes.

Coal-tar benzine is a readily inflammable, thin, volatile liquid, that leaves a transient fatty mark on paper, &c. The heavy vapours form

explosive mixtures with air, and still more violently explosive ones with oxygen. When treated with carriers of oxygen, like potassium permanganate and sulphuric acid, it takes fire spontaneously. When in the crystalline (solid) form, benzol (benzine) is also inflammable, and gives off inflammable vapours almost as readily as when in a liquid state.

Benzine readily becomes electrical (negative); see *Dry Cleaning*.

The remarks already made on ether and carbon disulphide equally apply to benzine, which, in point of fire and explosion risk, is intermediate between them.

Stringent regulations should be enforced with regard to the storage and use of benzine. Though dangerous as far as fire and explosion are concerned, it is not open to the aspersion of being spontaneously inflammable in a chemical sense, though it is often called so to cover negligence in working and non-observance of regulations.

Apart from the liability to ignite by electric sparks, none of the facts hitherto recorded in connection with benzine fires justify the assumption that benzine is really, and in a chemical sense, liable to ignite spontaneously.

The greatest danger presented, even by solid benzine, is in the vapour. Even at zero F. it throws off inflammable vapours which are highly explosive with air. Fortunately the limits of these explosive mixtures are very narrow, ranging only from 2.6 to 7 per cent. of benzine, the latter being the most dangerous. On account of the highly divergent composition of commercial grades of benzine, the explosion limits fluctuate very considerably. Beyond the figures mentioned the mixture ceases to be explosive, and merely takes fire.

Benzine explosions are more violent than many others, but, for the reasons specified, are much less frequent. The risk is ameliorated by the circumstance that the high density of the benzine vapours (greater than those of ether or carbon disulphide) retards their miscibility with air, the rate of diffusion being slow, and the vapour tending to accumulate in low-lying spots. On the other hand, this circumstance favours the tendency of the vapour to migrate, unless disturbed by a powerful draught; and in this manner the invisible cloud of benzine vapour may roll onwards until it reaches a distant fire where it ignites, and then produces at its point of departure explosions resembling those already described under *Explosions by Remote Fire*.

On this account all open fireplaces, lights, &c., the draught of which could exert any attraction on a cloud of benzine vapour, must be banished to a distance of not less than 50 feet from the place where the benzine is being used.

The density of the vapour increases the difficulty of ventilating rooms where benzine is used, the only effectual means being to instal a fan acting on the floor level, not at the roof. The rooms must be cut off from communication with all those on a lower level, *i.e.* there must be no intermediate stairways, shafts, openings for the passage of driving belts, lift shafts, ventilating tubes, or defects in the flooring. These precautions must always be adopted unless the benzine rooms are on the ground floor.

Benzol is prepared by distilling coal-tar or coking coal. The distillate passing over at 176°–190° F. is collected separately and cooled down to about 14° F. The benzol then deposited in the form of fern-like

crystals is pressed, and rectified in a column still. The process is one of considerable risk, and entails the most scrupulous care.

Benzine is used for a multiplicity of purposes, *e.g.* for dissolving fatty, oily, resinous, tarry, or waxy substances, caoutchouc, guttapercha, camphor, sulphur, iodine, bromine, phosphorus, or alkaloids. It is employed for extracting fat from bones, oil-seeds, wool, cleaning waste, &c. For this purpose benzol is safer than benzine, the latter often still containing volatile constituents to a greater extent than the purer but more expensive benzol.

Clothing, household linen, and gloves are often "chemically" cleaned with benzine, and the same solvent is used to recover fats from the waste waters of cloth- and wool-washing establishments, after converting the fat into a lime soap. Vermin in furniture, furs, and clothing are destroyed by means of benzine, though the articles thus treated become highly inflammable until the benzine has evaporated.

Benzine is also used for motors and for soldering lamps, one grade of fuel ("carburite") for motor cars consisting of benzol and spirit.

Detergent soaps and grease eradicators consist wholly or partly of benzine; rooms and courtyards are lighted with benzine; and the same liquid is used for carburetting gases of low candle-power, one ounce of benzine being sufficient to increase the illuminating value of 247 cubic feet of gas by one candle-power. On this account large quantities of benzine are consumed in gasworks and similar kinds of lighting plant. Use is also made of benzine, gasoline, &c., for heating combustion furnaces in laboratories unprovided with gas (see *Laboratories*).

The aniline industry employs enormous quantities of benzine for the production of nitrobenzol, and it is used to replace naphthalene in the manufacture of phthalic acid.

Rubber piping must never be used for conveying benzine or solutions containing same, since benzine corrodes them and makes them leaky; vulcanising the rubber is no advantage, the sulphur being also dissolved by benzine. Even pipes lined with canvas allow the benzine to leak through; and the assumption that a protective layer of sulphur is formed on the inner side is erroneous, as we have just seen. All pipes for conveying benzine should be as short as possible and made of metal, flexible metal piping of excellent quality being now obtainable.

Attempts have been made to solidify benzine, but without much success. In addition to gelatinised benzine (see later), endeavours have been made to produce a solid form of benzine by admixtures of diatomaceous earth (kieselguhr). This earth absorbs large quantities of benzine, which it afterwards gradually liberates again in the form of vapour—a behaviour that is utilised in carburetting gases and vapours, *e.g.* benzol lighting. The earth is, however, rendered extremely inflammable, and as it retains the final traces of benzine with exceeding tenacity, it must be handled with the greatest care for some considerable time after use.

In poker-work decoration on wood, use is generally made of a small benzine vapour lamp, and though the quantities in question are very small, the general precautionary regulations for benzine should be carefully obeyed.

The solvent power of benzine for fats is in inverse ratio to their rancidity. Hence, when it is a question of dissolving oxidised, resinified,

or rancid substances, the more powerful, though equally dangerous, disulphide should be employed.

In some cases benzine can be replaced by harmless materials, though this is rarely practised, either because of the greater expense, difficulty of recovery, or on account of the corrosive and insanitary character of these substitutes. However, they may be briefly mentioned here.

For the chemical cleansing of clothing, use may be made of ammonia or benzine soaps, both of which are harmless; good service is also rendered by gelatinised benzine, which is free from risk when used cold. This latter is prepared from soap, water, ammonia, and about 25 per cent. of benzine. On account of the small proportion of benzine the preparation must be warmed to about 176° F., a risky operation if carelessly performed. On the other hand, gelatinised benzine can be stored and handled without risk when cold; its employment diminishes the quantity of liquid benzine in use; the formation of explosive vapours is retarded; and the solid mass cannot be spilt about, a circumstance that of itself considerably decreases the danger.

The best of all substitutes for benzine is carbon tetrachloride, and this is now obtainable to any desired extent. It is sold as a grease eradicator ("Katharin"), is unflammable, furnishes no explosive vapours, and dissolves fat as readily as benzine. The boiling point being 170½° F., it can easily be recovered by distillation. The only drawback of this excellent and safe substitute for benzine is that it produces the same effect on the human organism as chloroform, its use being therefore objectionable from a hygienic standpoint. Another good, though not entirely harmless, substitute for benzine is light camphor oil (*q.v.*).

Where moderate quantities of sulphur, phosphorus, iodine, rubber, or guttapercha have to be dissolved, a comparatively safe substitute for benzine is afforded by chloroform, the price of which, however, prevents its employment in large amounts.

For nitrobenzol, see *Blasting Explosives*.

The recovery of benzine becomes an important question when large quantities are used; and, indeed, the method in which this recovery is effected is as important from the insurance companies' standpoint as the manner of using the benzine in the first place. The usual method of purification is by distillation; and the remarks made in connection with carbon disulphide are equally applicable to the present case, the risks being identical.

The recovered benzine is also decolorised and deodorised in order to fit it for use over again. Decoloration is effected with wood charcoal or bone black, both of which tenaciously retain traces of the benzine, and therefore remain dangerous for a considerable time after use, even though apparently free from benzine. These traces must be expelled by a careful application of (steam) heat, to prevent the occurrence of violent benzine explosions when the charcoal is subsequently recalcined. The steamed, spent charcoal must be stored in a fireproof manner, and generally treated in the way described under *Charcoal*.

The deodorising is effected with cottonseed oil, slaked lime, or with potassium bichromate and sulphuric acid, lead oxide, and soda lye being also used. The waste products containing benzine must be removed and treated with great care, the benzine being retained, both in the liquid

and gaseous state, for a very long time by these residues, which are mostly in the form of sludge.

The fact should be emphasised that deodorised benzine is just as dangerous as before, the smell having no influence on the risk.

In premises where the recovery of perfumes is effected by extraction with benzine, the vapours of the latter laden with the perfume are forced through sponges soaked with oil, petroleum, or glycerin, which absorb the perfume. The waste vapours should be conveyed safely to a fire-proof place, and not discharged into a flue; and the sponges must be protected from all risk of ignition.

Benzine fires break out very rapidly, spread at once, and easily set fire to other substances, &c. Where the benzine has become vaporised in closed rooms, explosions of the utmost violence are inevitable. As in similar fires of ether, oil, carbon disulphide, &c. (*q.v.*), water must not be used for quenching, though steam, carbon dioxide, ammonia, ashes, sand, or impregnated coverings are very serviceable on such occasions. In the event of fire in closed rooms, all apertures, even the ventilators, must be closed; open tanks, &c., containing burning benzine must be closed by means of tight-fitting covers, the arrangement being such that the covers can be slipped into position from outside. Care must be taken to provide a sufficient stock of the above-mentioned extinguishing agents in a dry state and close at hand.

The electrical behaviour of benzine merits special attention, electricity being, in most instances, the real cause of fires ascribed to the spontaneous ignition of benzine. As a matter of fact, benzine is not spontaneously inflammable in the chemical sense, but its vapours, when mixed with air, may be exploded by an electric spark.

Substances like cotton, linen, wool, silk, jute, oilcloth, especially unwashed or undyed wool or textiles, become more or less electrified when rubbed; and if the same materials be rubbed or even moved quickly about in a bath of benzine, or while soaked with benzine, the latter is also electrified (negatively, the substances themselves being positively electrified). Benzine being a bad conductor, the generated electricity accumulates, and reaches a tension which, as soon as ever an opportunity of equalisation arises, leads to the production of sparks and the ignition of the benzine. This is the true cause of the fires occurring in "dry cleaning" works, which fires were formerly a source of much speculation, and, in the absence of any other explanation, put down to spontaneous ignition. For a solution of the problem we are indebted to Dr. M. Richter, who performed numerous experiments with artificial benzine fires, and from whose work on the subject the following particulars are derived.

Richter attributes the primary cause of these fires to the electricity in the human body, which is transmitted by the hands of the workman to the material impregnated with benzine, this cause, and not merely the direct exchange of positive and negative electricity between the wool and benzine respectively, leading to the ignition of the last named. He also mentions the following important points:—

1. The presence of dry air in the benzine chamber favours electrical ignition by increasing the electrical tension. Hence it is desirable to charge the air of the chamber with moisture, so as to facilitate a timely and gradual equalisation of electricity. This result can be attained by

means of a small jet of steam. As a rule it is sufficient for the air to have a relative humidity of 70 per cent., *i.e.* to contain 70 per cent. of the total moisture it is able to take up at the prevailing temperature. A cubic metre (35·3 cubic feet) of air at 2° C. (35·6° F.) is able to take up 5·6 grams ( $\frac{1}{5}$  oz.) of water in the form of vapour, the quantity absorbed at 20° C. (68° F.) being increased to 17·2 grams. Hence, at the latter temperature, the presence of 70 per cent. of that quantity, or 12 grams ( $\frac{2}{5}$  oz.) of water will render the air sufficiently humid (see *Oilcloth*). In order to determine the humidity of the air, the use of a good hygrometer should be made compulsory.

2. Fibres and textiles are partly deprived of their susceptibility to electrical excitation by being warmed to 105°–120° F., and by the operations of dyeing and finishing; and in that condition are therefore less prone to ignition than when undyed and unwarmed.

3. Since warm air is generally more fully saturated with moisture than cold air, the winter is a more dangerous season than the summer.

4. Above 21 $\frac{1}{2}$ ° F. benzine almost entirely loses its power of becoming electrified. Used and repurified benzine behaves like the perfectly fresh substance.

5. The purer the benzine, the lower its tendency to electrification; and chemically pure benzine (benzol) has only a very slight susceptibility in this respect.

6. Dust acts like moisture; dusty air conducts accumulated electricity away more rapidly than air devoid of dust, and therefore prevents the attainment of a high tension.

7. According to Richter, fragments of metal (buttons, edgings, and decorations on the fabrics) favour ignition, though not directly producing same. The same applies to the metallic fittings of the apparatus, and that too in a manner productive of great anxiety.

8. The aforesaid preventive precautions are not always practicable. Humid or dusty air may spoil the finer goods under treatment. Moreover, it is not merely sufficient to remove the electricity from the fabrics, benzine, and apparatus, the electricity derived from the human organism having also to be borne in mind.

9. The sole means of preventing the ignition of benzine under these circumstances is by suppressing the generation of electricity, by using Richter's "antibenzinpyrine," the addition of as little as 0·10 per cent. of this substance to the benzine having the desired effect.

Similar agents, composed of anhydrous soft soap or magnesia soap, have already been tried with equally good results.

10. Vegetable fibres exhibit a lower tendency to electrical excitation than those of animal origin.

11. The question whether the presence of fat favours the production of electricity and influences the occurrence of benzine fires, has not been sufficiently investigated.

In accordance with the principles laid down by Richter, the following list may be compiled of the influences favouring and retarding the production of benzine fires by electrical ignition:—

Unfavourable.	Favourable.
High degree of atmospheric humidity.	Dryness of air and fabric.
Previous warming of the fabric.	Cold fabrics.
Dyeing and repeatedly washing the fabric.	New, undyed fabrics.
Large amount of dust in the air.	Absence of dust.
Hot air.	Cold air.
High benzine temperature.	Cold benzine.
<i>I.e.:</i>	<i>I.e.:</i>
Warmth and moisture.	Cold and dryness.

The conditions are very similar in oilcloth factories (*q.v.*), in which large quantities of benzine are used and vapours liberated.

The solution of rubber in benzine, so largely used in rubber works, is not particularly dangerous so long as it is in the gelatinous state, the benzine contained in the swollen rubber having lost nearly the whole of its volatility, and therefore giving off only a minimum of vapour. The mass is ignitable and combustible, but does not become dangerous until spread out thin, or warmed to such a degree that the benzine is expelled; or, finally, when the solution is diluted with benzine to a fluid condition, in which event the risks are the same as for benzine alone.

To get rid of the benzine from the treated fabrics, &c., they are placed in a centrifugal separator. In this case, also, electrical excitation occurs, and dangerous explosions may ensue from the large amount of benzine vapour disengaged by the high speed of the separator.

## CHAPTER XLV

### TOLUOL (Methylbenzol)

Sp. gr. 0.881. B.p. 231 $\frac{3}{4}$ ° F.

THIS readily inflammable liquid is present in impure benzol, which it resembles and which it accompanies as a coal-tar product. It is, however, far less dangerous from fire or explosion than benzol, and can be judged less severely. Toluol vapour forms explosive mixtures with air, the maximum effect being reached at 7 per cent. For the nitro-compounds of toluol, see *Blasting Explosives*.

Of the natural products containing mineral oils, there remain to be mentioned asphalt and ozokerite.

## CHAPTER XLVI

### ASPHALT

IN addition to natural asphalt (asphaltic rock, mixed with lime, clay, and shale; mountain tar (soft), mountain pitch, Syrian bitumen), there

is an artificial asphalt (German asphalt, coal-tar pitch, compressed asphalt, tar pitch, bituminous mastic, asphaltic mastic, goudron).

Natural asphalt has the sp. gr. 1.100–1.200, melts at 212° F., forms an almost coal-black mass, and contains volatile oils furnishing inflammable vapours exploding on admixture with air. To eliminate these substances the asphalt has to be warmed to 340°–445° F. until all the volatile oils have been driven off. This operation is dangerous, but the resulting asphalt is far safer than before. Well-purified asphalt should not lose more than 2 per cent. in weight when heated to 437° F. for six hours, any greater loss indicating imperfect purification and correspondingly increased danger. Most of the agents employed for dissolving asphalt are dangerous (benzol, petroleum, carbon disulphide, and ether, though the latter is merely a partial solvent), and hence the resulting solutions are dangerous to handle. A special warning must be uttered with regard to the inflammability and consequent ignitibility of asphalt when applied to any surface.

Though inflammable, asphalt does not burn with readiness; nevertheless, burning asphalt forms a very dangerous disseminator of flame, the more so because it is difficult to extinguish. All articles that have been coated with asphalt, more particularly as a protection against moisture and decay, thereby acquire a high fire risk. The application of asphalt for this purpose to felt, timber, millboard, paper, textiles, fibrous materials, and the like, and also as a preventive of rust on metals, must therefore be performed away from any open fire when a solution of asphalt is used. When, however, the asphalt is softened by warmth, then a fireplace is indispensable. The heating and treatment of asphalt for large street works and the like must be carried on out of doors, far enough away from any inflammable objects, and only when a sufficient stock of sand, earth, or ashes is available for use in the event of fire.

Purified asphalt is moulded into plates, a temperature of 340°–390° F. and a pressure of (up to) 200 atmos. being required. In laying down asphalt paving in the street, the danger of the operation is diminished by the addition of sand and gravel to the asphalt melted at 250°–340° F.

When of sufficient thickness, such a layer of asphalt is able to delay the spread of fire, momentarily at least, being a very bad conductor of heat and therefore protecting combustible objects from the heat of the fire. A moderately thick flooring of asphalt (with admixtures) will greatly retard the passage of a fire either from above or below; it does not crack under the influence of heat, but rather tends to expand; it takes fire slowly, and is really safer than cement, the latter crumbling when strongly heated.

In one case of fire it was found that the asphalt flooring remained as a coherent mass long after the wooden joists had burned away, and finally fell, without breaking, into the room below, thus putting out the fire. It, however, proved less suitable for pillars, a short exposure to heat sufficing to soften the mass, which then lost its bearing strength and soon allowed the supported floor to collapse.

Asphalt consequently behaves in three different ways in presence of fire:—

Spreading flame when applied as a thin coating on objects;

Preventing the transmission of heat, when as a compact mass in walls and floors ;

Dangerous and of no bearing strength, when as a compact mass in the form of pillars.

The common practice of adding oil of turpentine to asphalt, before or after melting same, may easily result in spontaneous ignition (see *Turpentine*).

The term "artificial asphalt" is of broad application, and it is therefore a somewhat difficult matter to give any definite information on the behaviour of these products in presence of fire.

Artificial asphalt may be a mixture of natural asphalt with coal-tar residues ; a mixture of graphite, shale, ground asphalt, and heavy petroleum oils ; a mixture of distillation residues from petroleum, lignite, and resin, with sulphur and adjuncts like sand and gravel ; a mixture of tar, sulphur, and slag. Owing to the necessity for heating the, often dangerous, ingredients to 320°–390° F., the preparation of artificial asphalt is always attended with danger.

Generally speaking, artificial asphalt must be classed as more dangerous than the purified natural product, though probably about on a par with the impure natural asphalt, owing to the presence of heavy oils and tars that, equally with the latter, give off volatile and inflammable vapours.

When used for walls and flooring, the artificial asphalts are less able to resist fire than the natural product mixed with adjuncts. Hence their use is more confined to the manufacture of lacquer, lampblack coating paper, wood, pipes of all kinds, and as a protective coating against rust, the fire risk imparted to the treated articles being at least as great as in the case of natural asphalt.

## CHAPTER XLVII

### OZOKERITE (Mineral Wax, Ceresin, also often called Paraffin)

Sp. gr. 0.94–0.95.

THE melting point varies considerably (68°–140° F.) according to the origin and purity ; ceresin, or refined ozokerite, melts at 167°–176° F.

In point of danger natural ozokerite is about on the same plane as crude petroleum ; the fire risk of ceresin is equal to that of the fats. Ozokerite may give rise to explosions ; ceresin chiefly favours the spread of flame.

Both crude and refined ozokerite are combustible and easily inflammable. On distillation at 570° F. the former yields inflammable oils and vapours. It is purified by re-melting, then refined by treatment with concentrated sulphuric acid and ferrocyanide residue. The operation is performed at 355°–390° F., and is dangerous on account of the explosive vapours produced.

Even the mere storage of crude ozokerite is attended with danger,

owing to the presence of 3-8 per cent. of petroleum ether, which is highly volatile and may render explosive the air of closed rooms. For this reason the storerooms must be well ventilated, properly sheltered from ignition, and must not be visited with naked lights or heated with open fireplaces.

The dangers of ozokerite refining are about on a par with those of resin distilling, except that larger quantities of ozokerite are refined at a time, *e.g.* up to 3 tons a day. Special danger may arise during the process if the lumps of ozokerite do not cover the floor of the heated still uniformly all over, and local overheating therefore ensues. In such event the overheated ozokerite will liberate benzine vapours, which may then give rise to very dangerous explosions (as in the case of resins).

Wrought iron is the only suitable material for the pans, cast iron being liable to crack and let the melted ozokerite run through into the fire, with serious results. The pan bottom should not be directly touched by the flame, and great care must be exercised in firing. The temperature must be carefully controlled by the aid of good and clearly legible thermometers, and should not be allowed to rise above 390° F. The proviso as to the legibility of the thermometer is necessary, so that there shall be no need for the workmen to resort to the dangerous practice of using lighted matches or open lamps in order to read the temperature. Other conditions also essential to minimise the risks of the process are: the provision of efficient stirrers, to prevent the mass charring at the bottom of the pan; well-fitting covers, for use in the event of a pan fire; overflow gutters to all the pans, for safely carrying away any of the contents that may froth over, a not infrequent occurrence on the addition of the neutralising powder; and a sufficiency of dry sand to throw over any burning ozokerite or ceresin.

Special attention must also be devoted to the waste products, which are mostly of a fatty nature: press residues, press cloths, filtering paper, and even the light dust out of the flues, are all liable to spontaneous ignition and must be stored in a fireproof manner, quickly removed and rendered innocuous.

The danger is heightened by the use of benzine for recovering the ozokerite and ceresin waste, large quantities of the solvent (*q.v.*) being required for this purpose. Hence the whole plant is subject, in a high degree, to risk of fire and explosion.

The purified ceresin is attended with the same dangers as wax or fat. It is used for a variety of purposes, especially as a substitute for beeswax, for artificial honeycomb, candles, wax figures, and polishes.

Where dissolved ozokerite or ceresin is used the nature of the solvent must be ascertained, since on this depend the danger of the solution and the kind of vapours evolved. The solvents here in question include benzine, carbon disulphide, oil of turpentine, and fatty oils.

## CHAPTER XLVIII

## TAR

THERE are several varieties of tar: wood tar, peat tar, shale tar, lignite tar, and coal tar or gas tar, the name indicating the raw material used in each case. All these products are obtained by simple dry distillation.

One and the same kind of tar may vary considerably in composition, and on this account it is impossible to arrange the tars in the order of their relative risk. The dimensions of that risk depend in each case on the percentage content of readily volatile gases and vapours; should these exceed 2 per cent., the tar may be inflammable as low as 118° F. and the vapours be explosive; whereas if these 2 per cent. be eliminated, the flashing point rises to about 180° F.

If the highly variable sp. gr. be taken as a criterion of the inflammability and danger of the tar, the highest place is taken by peat tar, 0·896–0·965, this being followed by lignite tar (0·88–1·0), wood tar (1·075–1·160) and coal tar (1·15–1·220) last.

The various tars possess many constituents in common, though each of them has one or more specially characteristic substances, as the following table will show:—

Wood tar: *creosote, acetic acid, wood spirit*; also benzol, cresol, cumol, toluol, xylol, paraffin, pyrogallie acid, and ammonia.

Peat tar: the constituents of wood tar; also, in smaller amount: carbolic acid, valerianic acid, propionic acid, sulphuretted hydrogen gas, asphaltum, ethylamine, aniline, and hydrogen cyanide.

Lignite tar: *paraffin, photogene, solar oil*; then benzine, gas oils, paraffin oils, lubricating oils, creosote, and empyreumatic resins.

Shale tar: same as lignite tar.

Coal tar: *benzol, toluol, carbolic acid, naphthalene, tar oils, pitch*; then: naphtha, cresols, aniline, anthracene, and phenanthrene.

The substances indicated by italics form the main constituents in each case. The principal industrial uses of each tar are given below:

For the recovery of:

Pitch, lampblack, creosote—Wood tar;

Lamp oils, paraffin, asphaltum—Peat tar;

Paraffin, photogene, solar oil—Lignite tar;

Benzol, toluol, carbolic acid, naphthalene, tar oils—Coal tar.

The last two tars differ in respect of their naphthalene and paraffin content.

The following table of coal-tar products shows the serial order in which they distil over as the temperature rises, their uses being also indicated:—

Temperature.	Name of Distillate.	Contents.	Employed in the Production of
(a) 221°-230° F.	First runnings (spirit)	Water, ammonia, gassy tar oils	Ammonia salts.
(b) 230°-338° F.	Light oil (benzine oil)	Crude benzol  Solvent naphtha	Benzol, toluol, xylol, dye-stuffs. Grease eradicators, dry cleaning (benzine), varnish, lacquers, caoutchouc solution, carburetting.
(c) 338°-464° F.	Medium oil (carbolic)	Carbolic acid  Naphthalene	Carbolic acid, salicylic acid, dyestuffs, disinfectants, impregnation. Phthalic acid, benzoic acid, lighting, preservatives.
(d) 464°-518° F.	Heavy oil (green oil)	Cresols, naphthalene, liquid paraffin	This mixture is generally used up as a whole for cart grease, fuel, lighting material, impregnating wood or ropes, making lamp-black, or softening pitch.
(e) 518°-572° F.	Anthracene oil	Crude anthracene, paraffin (little), phenanthrene, chrysene	Anthracene, dyes, alizarin, paraffin candles.
(f) ...	Residue, pitch	Soft pitch, hard pitch	As a protective paint against damp and rust. For artificial asphalt, briquettes, varnish, lacquer, lamp-black. With heavy oil (d) as a tar substitute for painting wood, wooden roofs, paving blocks, &c.

Tar distilling is a dangerous operation, whether on the large or small scale:—

1. On account of the inflammable gases furnished by the tar, *e.g.* methane, ethane, ethylene, acetylene; and when gently heated, volatile oils of a highly inflammable and explosive character, like naphtha and benzol. Birch tar contains a good deal of methyl alcohol and acetone.

2. By reason of the large quantity of tar treated at a time, often as much as 25 tons.

3. Because, at the commencement of distillation, and therefore when highly laden with the most dangerous substances, the tar readily froths over, boils with apparent violence, and bumps in an explosive manner, birch tar being the worst in these respects.

4. Because the pipes are liable to choke up towards the end of the distillation, and thus set up in the apparatus high pressures that may lead to explosions.

5. Because the free, fine carbon abundantly present in the tar, settles on the bottom of the apparatus to a kind of incrustation, which leads to overheating in the same way as boiler fur in ordinary boilers.

6. Because a species of lampblack (*q.v.*), of a highly inflammable nature, is deposited in the still dome.

7. Because the ammonia water in the first runnings strongly corrodes the dome, rivets, and rivet holes of the still, and so weakens the vessel in

the course of 3-5 years, as to render it liable to burst and liberate a large volume of dangerous gases and vapours.

For the first two dangers there is no remedy, but the others may be to some extent diminished by the following precautions:—

No. 3, by carefully freeing the tar from water previous to placing it in the still. This entails heating for several days at  $212^{\circ}$ – $245^{\circ}$  F. A new method of preventing frothing, invented by Ostrejko, consists in blowing steam through a funnel-shaped pipe that debouches just above the surface of the tar (but without touching it), so that the bubbles are broken up as soon as formed.

No. 5, by the use of efficient stirrers, chipping off the coke deposit in good time, and protecting the still bottom from overheating by means of a brick dome.

No. 6, by abolishing all fittings likely to form a resting-place for the fine carbon (see 7).

No. 7, by allowing the dome supports to project about 6 inches in the interior of the still, so as to prevent the ammonia water trickling down the walls (rivets and rivet holes); at the same time, the whole must be arranged in such a manner as to prevent the deposition of fine carbon at these places (see 6).

Even when distillation is ended, there is the possibility of an explosion being produced by the dangerous gases (partly carbon monoxide) escaping during the withdrawal of the pitch residue.

Here the employment of any naked flame is a source of danger; and the same remark also applies to the introduction of a light into the emptied stills, or indeed in any vessel that has contained tar or its distillates. The use of naked lights for this purpose must therefore be strictly prohibited.

Since the recognition of the high value of the constituents of tar, that substance itself is no longer put to its original uses, but is replaced for this purpose by a mixture of tar pitch and heavy tar oil. This mixture, which is free from the most volatile, and therefore most dangerous constituents, is safer than the original tar, its explosive tendency being reduced to almost nil, though it still remains inflammable and capable of spreading fire.

The use of tar as a paint or impregnating medium is a somewhat dangerous operation, since it necessitates the employment of temperatures up to about  $392^{\circ}$  F. (generally over open fires), at which inflammable vapours are liberated, or else the tar is thinned down with volatile diluents, which render it still more inflammable. This diluted tar, when spread out thinly on any surface, liberates a large quantity of inflammable vapours and tar gases, which may lead to violent explosions, especially in a closed room.

A liberation of dangerous tar gases during the conveyance of the crude tar from place to place, is also an imminent contingency, from the vibration and heat (sunlight) to which the material is exposed.

Large stocks of tar should be sheltered from the sun (tar barrel explosions). The only materials suitable for extinguishing tar fires are sand, ashes, and earth, though, when the fires occur indoors and the supply of air can be cut off, good service may be done by the introduction of stifling gases or vapours: carbon dioxide, hydrochloric acid, steam, ammonia, or sulphur dioxide. In the absence of these, an attempt should at any

rate be made to exclude the air as completely as possible. Water should only be used with great caution, since some tars and certain tar constituents are lighter than water, and where an insufficient amount is used the sole result may be to spread the burning tar. In fact, the use of water for extinguishing tar fires is only advisable when the supply is abundant and the local conditions otherwise favourable. These remarks apply in general to all tars.

Owing to the special classification of the distillates of lignite tar, the following table has been compiled for the purpose of comparing them with the distillates furnished by petroleum and coal tar respectively:—

Lignite Tar Distillates.	Specific Gravity.	Flashing-Point.	Boiling-Point.	Approximately Corresponding Distillates from	
				Coal Tar.	Crude Petroleum.
Benzine I. . . .	0.742	Degs. F. 20	Degs. F. 159	First runnings (spirit)	Petroleum ether, gasoline, benzine, ligroin.
Benzine II. . . .	0.770	43	212	...	...
Lamp oil I. . . .	0.788	86	260½	Light oils (benzine oil)	Cleaning oil.
„ II. . . .	0.803	122	307½	...	...
„ III. . . .	0.819	160	370½	Medium oil	Lamp oil (kerosene).
„ IV. . . .	0.836	201	419	Heavy oil (green oil)	...
Cleaning oil . . .	0.848	223	426	...	...
Gas lubricating oil . . . .	0.878	242½	492-590	Anthracene oil	Lubricating oils, paraffins.

Tar furnishes two solid products of special value, namely:—

Naphthalene, chiefly derived from coal tar.

Paraffin, mainly obtained from lignite.

Of these, the greater fire risk is exhibited by naphthalene.

## CHAPTER XLIX

### NAPHTHALENE (Coal Tar Camphor)

Sp. gr. 1.150. M.p. 174° F. B.p. 424½° F.

NAPHTHALENE is obtained by distilling medium coal-tar oil at 410°-446° F., as a white mass, readily combustible, volatilising easily, and frequently contaminated with dangerous light oils.

Impure naphthalene is highly dangerous, and even in the pure state it is attended with danger, on account of the inflammability and explosibility of the vapours it liberates at the ordinary temperature. It

also explodes on contact with flame or sparks, when disseminated through the air in the form of floating dust.

An indirect explosion risk is produced by naphthalene by choking up the pipes through which it is passed on preparation or use, if the same be allowed to cool down too low. Under these conditions the naphthalene is deposited as a hard mass, and thus exposes the apparatus to a pressure that greatly augments the risk of an explosion of the still uncondensed vapours. This contingency is specially imminent in the sublimation apparatus for purifying naphthalene, and therefore it is always essential to see that the pipes are kept sufficiently warm.

Naphthalene is put to a variety of uses. As a preventive of vermin in stuffed animals, clothing, wool, fibrous materials, yarns, textiles, furs, its vapours are disseminated throughout the material, adhere firmly, and even if not imparting direct risk of ignition thereto, make the same more combustible than before. In such cases a spark is sufficient to set the material alight, the air impregnated with naphthalene vapour assisting the further progress of combustion in a manner analogous to that of camphor vapour and oxygen.

This danger becomes intensified in natural history collections, furriers' stores and stores of textiles, yarns and woollen goods, it being usual to add naphthalene by the pound to large shipments of such goods.

Since naphthalene vapours burn with a very bright flame, and also intensify the brightness of other flames (*e.g.* coal-gas), this substance is used as a carburetting agent. An example of its use in this direction is afforded by the Albo-carbon light (*q.v.*), which is generally safe enough under good management; but if carelessly looked after, and the naphthalene allowed to get overheated, may be attended with the risk of naphthalene explosions.

Other uses of naphthalene are in the dye-stuff industry, the manufacture of lampblack, and the preparation of chemicals, *e.g.* phthalic acid, naphthol, benzoic acid. The liberation of vapour is especially liable to occur in the phthalic acid process, owing to the high temperatures employed (355°–390° F.) and the presence of substances giving off oxygen, *e.g.* potassium chromate and sulphuric acid as oxidising agents. The presence of oxygen always increases the explosion risk of combustible vapours, and the danger is often heightened by the substitution of benzol for naphthalene.

Treated with nitric acid it furnishes nitronaphthalenes, which merely detonate slightly when heated, but are otherwise attended with little danger. These nitronaphthalenes must not be confounded with the explosive nitronaphthols and dinitronaphthols largely used in yellow dyeing.

## CHAPTER L

### PARAFFIN (Lignite-tar Camphor)

Sp. gr. 0.869–0.843. M.p. 84°–158° F. B.p. 572°–752° F.

Flashing point, 323½° F. Burning point, 316°–383° F.

CHEMICALLY speaking the name paraffin is applicable to a whole series of hydrocarbons; but here we have only to deal with the chief representative of that group, the ordinary paraffin scale. Liquid paraffins are

also known. These wax-like, combustible substances are chiefly recovered from lignite tar, but also from bituminous shale, petroleum, and ozokerite.

The recovery of paraffin is a very dangerous operation on account of the accompanying by-products, benzol, paraffin-oils, and gas-oils (see also *Candle-Making*), and explosions are not impossible.

Paraffin itself is not very dangerous when pure, being then on a par with the fats, with which it has in common the properties of ready fusibility, inflammability, and tendency to spread flame. The risks are greater when the paraffin is impure; the greater the impurity the softer the scale, and therefore the lower the melting and flashing points, these being depressed by the presence of more inflammable substances.

Paraffin melting at 84°	F. flashes at 316½°	F.	} these are termed "soft paraffin"
" " 91½°	" " 323½°	"	
" " 100½°	" " 334½°	"	
" " 115°	" " 359½°	"	
" " 122°	" " 377½-383°	F. "hard paraffin."	

A considerable amount of inflammable vapour is given off at 212° F.; in fact, at this temperature 16 per cent., or nearly one-sixth of the whole mass of the paraffin, is converted into vapour.

For use paraffin is generally prepared by treating it with solvents, rather than by the aid of heat; and as these solvents are mostly of a dangerous nature (petroleum ether, carbon disulphide, and benzol), all open fires and lights must be kept at a safe distance on account of the vapours liberated by these liquids on evaporation.

Paraffin is largely used as a coating and impregnating medium for protecting walls and other objects from damp, rust, or decay. Vessels and tools are coated with or dipped in paraffin to make them proof against acids or alkalis.

The faculty of paraffin for readily transmitting flame is utilised in the manufacture of Swedish matches, which are impregnated with that substance in order that the matchsticks may burn more readily. In this instance paraffin takes the place of the sulphur in phosphorus matches.

Paraffin is also largely used in candle-making (*q.v.*); also for feeding lamps for glass-blowing; as a heating and cooling medium in heating and cooling baths, and as a substitute for wax in satinising.

When heated along with sulphur, paraffin liberates the inflammable (and sometimes explosive) gas, sulphuretted hydrogen (*q.v.*)

# PART IX—DANGERS PRODUCED BY ALCOHOLS, ETHERS, AND OTHER LIQUIDS

## CHAPTER LI

### I.—ALCOHOLS

ALCOHOL is a generic term, and applies to a large series of organic compounds consisting of carbon, hydrogen, and oxygen, and having the same fundamental chemical composition. The chief member of the series is spirits of wine, which is called alcohol when chemically pure and of a certain degree of strength.

The alcohols are for the most part liquid and volatile, only a few—*e.g.* mannite and erythrite—being solid and non-volatile.

They are generally combustible, some of them readily inflammable; and though perfectly safe alcohols are not unknown, the name "alcohol" is associated with the idea of inflammability and fire risk, and to a certain extent also with that of explosion (especially when warmed alcoholic vapours are in question). For this reason very stringent precautions should be prescribed for all premises where alcohol is employed.

Alcoholates are chemical compounds of alcohols and salts like calcium chloride and magnesium sulphate, wherein alcohol plays the same part as water of crystallisation. Alcoholates are free from any particular danger, and in this respect are not to be compared to the alcohols themselves.

Alcoholising a substance merely implies reducing the same to a state of extremely fine division, not treating it with alcohol; and an otherwise harmless substance is not therefore converted into a fiery one by this process.

#### 1. Alcohol (Alcohol Absolutus, Absolute Alcohol, Ethyl Alcohol, Ethyl Hydroxide, Methylcarbinol, Spirit of Wine)

Sp. gr. 0.794. B.p.  $172\frac{1}{2}^{\circ}$  F. Solidification point,  $-202^{\circ}$  F.

Vapour density, 1.613.

Alcohols of different strengths gives off inflammable vapour at the following temperatures:—

Absolute alcohol at $51^{\circ}$ F.	40 per cent. alcohol at $78\frac{3}{4}^{\circ}$ F.
80 per cent. „ $68^{\circ}$ „	30 per cent. „ $85\frac{5}{8}^{\circ}$ „
70 per cent. „ $69\frac{3}{4}^{\circ}$ „	20 per cent. „ $97\frac{1}{4}^{\circ}$ „
60 per cent. „ $71\frac{1}{2}^{\circ}$ „	10 per cent. „ $120\frac{1}{4}^{\circ}$ „
50 per cent. „ $75\frac{1}{4}^{\circ}$ „	5 per cent. „ $143\frac{1}{2}^{\circ}$ „

The final limit of inflammability is only attained between 5 and 3 per cent.

Strong alcohol will ignite readily even in the cold; but for that of 60 per cent. strength a temperature of  $80\frac{1}{2}^{\circ}$  F. is necessary, and  $87\frac{3}{4}^{\circ}$  F. for 45 per cent. spirit.

Alcohol of 99–99 $\frac{1}{2}$  per cent. strength is classed as alcohol, that of 95–97 per cent. as fine spirit, that of 80–86 per cent. as raw spirit, and that of 80 per cent. strength as burning spirit.

Alcohol is generally highly inflammable; when mixed with water it generates but little heat and therefore its inflammability is diminished. When mixtures of alcohol are distilled the alcohol passes over first, and the distillates are stronger in alcohol than the original liquid. In consequence of the hot vapours given off, the distillation of even weak alcohol is not free from risk, these vapours being explosive as well as inflammable. The following table shows the percentage of alcohol in the vapour produced by distilling various mixtures of alcohol and water:—

Mixtures with—	1	2	3	5	7	10	12	15	20	30	40	50	60	70	80
per cent. of alcohol.															
Vapour with—	13	28	36	42	50	55	60	66	68	71	78	85	87	89	90 $\frac{1}{2}$
per cent. of alcohol.															

If the vapours from the 1 per cent. mixture, and therefore containing 13 per cent. of alcohol, be warmed to  $176^{\circ}$  F., they become inflammable.

Alcohol between 60 and 99 $\frac{1}{2}$  per cent. strength is more inflammable than ordinary petroleum (f.p.  $70^{\circ}$  F.); but, on the other hand, the vapours are far less explosive, since to attain this condition they require to be strongly heated and placed in contact with a flame or electric spark. In point of general fire-risk, alcohol is far below ether, benzol, carbon disulphide, and similar liquids.

Special danger attaches to alcohol by reason of its high diffusibility. With the exception of glass and metals there are few substances through which alcohol is unable to penetrate, even when of only 60 per cent. strength. It will pass through animal bladder, especially when the external air is damp, the loss amounting to 40 per cent. of the alcohol in thirty days. Neither wooden vessels nor the most compact cement tanks, &c., can prevent escape, and the stronger the alcohol the quicker the dispersion.

Though this escape proceeds only gradually, and therefore seldom leads to direct dangers, it is nevertheless worthy of mention as an evidence of the necessity of great care in the choice of material for storage vessels. Not only does alcohol diffuse easily, but it readily leaks when mixed with water, and this constitutes a source of grave danger. Large vessels for storing alcohol, even when set in brickwork, must be mounted in such a manner that any leakage will be detected at once. For explosions in spirit tanks, see *Tanks*. The use of fire in repairing these vessels must not be permitted until the whole of the residual traces of spirit have been expelled by ventilating and swilling out the vessels.

In admixture with certain substances alcohol generates heat, which may lead to flashing and even ignition: *e.g.* concentrated sulphuric acid, fuming nitric acid, metallic potassium or sodium, permanganic acid, and per-acids generally.

With nitric acid in presence of silver or mercury, it furnishes the

dangerous fulminates of these metals; and when gently warmed with nitric acid alone it gives a very violent reaction and dangerous products. With sulphuric acid it furnishes the readily inflammable liquid ether (*q.v.*), and with metallic potassium or sodium the explosive gas hydrogen (oxyhydrogen gas).

Of late a solidified form of alcohol has been put on the market. This solid spirit renders the employment of alcohol safer, provided the mass does not drip or melt in time or when warmed to 86° F.; otherwise it is just as dangerous as liquid spirit, and even more so, because reliance being placed on the assumed safety of the preparation, it is handled with less care (see *Solidified Petroleum*).

The means adopted for rendering solidified alcohol less volatile and dangerous, consist in either coating it with some protective medium like sodium silicate (water glass), or absorbing the melted preparation with some porous substance, such as kieselguhr. This latter material will also absorb two to three times its own weight of ordinary liquid alcohol, thus forming a species of solid spirit; but too much reliance should not be placed on this preparation, since no actual solidification of the spirit is effected.

Among the more dangerous forms of solidified spirit may be mentioned those prepared from nitrocellulose, and such as contain cheap, impure benzol in addition to alcohol. Solidified spirit is also made into candles, which, in addition to spirit and soap, also contain nitrocellulose, wood charcoal, lycopodium, sawdust and cotton waste, and are wrapped in paraffined paper or tinfoil. These preparations are not without objectionable features.

Up to the rectifying stage, the production of alcohol from saccharine materials, by fermentation and distillation, is free from risk, danger only commencing when the alcohol has become concentrated by the various operations in the distillery. In one process it is freed from water and certain impurities by the action of quicklime and wood charcoal. Here, all the precautionary regulations for dangerous establishments should be observed, more particularly the prohibition of all naked lights; the alcoholic waste products must be carefully stored away, and all vessels containing spirit kept closed. There are few premises but use alcohol for some purpose or other, though, as it is generally in a diluted condition, the risk is small. The most extensive application of spirit is in the preparation of extracts, tinctures, lacquers, varnishes, colours, vinegar, chloroform, ether, alkaloids, scents, liqueurs, and pharmaceutical articles; also as a solvent for various substances, for charging thermometers, for cleaning, heating, boiling, lighting, and preservative purposes.

To cheapen alcohol for technical purposes, it is *denatured*, generally with methyl alcohol (2 per cent.), which, however, increases the risk of fire and explosion, owing to the rapidity with which the adjunct evaporates, and to the explosive vapours it yields. When this *methylated spirit* is burned in lamps, an accumulation of these explosive vapours may be easily formed in the container, igniting and exploding when the lamp is lighted. Frequent instances of this kind have been known in practice.

Rubber pipes or tubing made of organic materials should never be used for conveying alcohol, or connecting vessels containing that liquid,

when the strength of the spirit is above 50 per cent. Flexible metallic tubing, which is now made of good quality, is necessary in such cases.

Among spirituous liquors, only such as are rich in alcohol are dangerous, and even then the risk is not high, since it is only when they are in a warm and undiluted condition that they readily ignite. Inflammable vapours are liberated by: Ordinary brandy, at  $84^{\circ}$  F.; Dutch gin at  $89\frac{1}{2}^{\circ}$  F.; whisky at  $82\frac{1}{2}^{\circ}$  F.; rum, arrack, and cognac at about  $77^{\circ}$  F., according to strength; and by sherry and port wines at  $129^{\circ}$  F.

## 2. Methyl Alcohol (Wood Spirit, Methyl Hydroxide)

Sp. gr. 0.814. B.p.  $152^{\circ}$  F. Flashes at  $32^{\circ}$  F. (or, according to Raikow, at  $49^{\circ}$  F.). Vapour density, 1.120.

This liquid resembles ethyl alcohol in many respects; but the vapours are more volatile, easily inflammable, and are explosive at the ordinary temperature owing to their content of acetone.

It is used for denaturing alcohol (*q.v.*), which, however, it renders more inflammable; and is also used for purposes for which spirits of wine are too expensive.

In the impure state (wood spirit) it is far more dangerous than when pure, owing to the presence of acetone (*q.v.*) in large amount. This impure wood spirit (wood vinegar) varies considerably in composition, has the sp. gr. 1.013–1.030, and is largely used for preserving meat by smoking, in dyeing, in the manufacture of vinegar and acetates, as a plumping soak in tanning, and for disinfection (see *Formaldehyde Lamps*).

Methyl alcohol is recovered from the products of the dry distillation of wood. The gases and vapours liberated in this operation are inflammable and explosive. The products are rectified in column stills, occasionally over quicklime, acetone being recovered as a by-product. Owing to the risk of vapour explosions, especially in presence of naked flame, the process entails great caution.

With potassium or sodium it liberates hydrogen and oxyhydrogen gas (explosive).

## CHAPTER LII

### II.—ETHERS, COMPOUND ETHERS, MIXED ETHERS, FRUIT ETHERS

LIKE "alcohol," the term "ether" is a generic appellation for a large series of organic compounds of definite composition. The chief representative of the group is sulphuric ether, commonly known as ether.

The ethers are usually volatile, readily inflammable and combustible, far more so indeed than the alcohols, from which latter they differ in the explosive character of their vapours at low temperatures, alcohol vapours being explosive only when hot.

The ethers usually have lower boiling points than alcohols, there being but few exceptions to this rule.

Wherever large quantities of ether vapour are liberated, great danger of explosion is imminent.

Ethers are generally prepared by distilling alcohols with the corresponding acids or salts and in presence of sulphuric acid. In some cases the reaction is so violent and so much heat is generated that the ethers distil over of themselves, in which event artificial heating must be avoided. Hence the process is more or less dangerous, and entails thorough cooling and a careful mixing of the materials.

## 1. Ether

(Ethyl Ether, Ethyl Oxide, Aether Vitrioli, Aether Sulfuricus, Naphtha Vitrioli, Vitriol Ether (or Naphtha), Sulphuric Ether, Vinous Ether).

Sp. gr. 0.720. Vapour density, 2.560. Boils at 95° F. (the commercial grade at 100½° F.) Flashing point, -4° F.; burning point, -4° F.; solidification point -24° F.

Ether is an extremely volatile and inflammable liquid, the vapours of which form highly explosive mixtures with air.

When heated, it has a great tendency to boil over, like milk, and then ignites in contact with a flame. Hence ether must never be heated over direct fire, but only over hot water, in an air bath or by steam. When the ether contains solid substances (powders, &c.), which it is being used to extract, the danger is accentuated, the finer the substance the greater the tendency to boil over. A similar overflow occurs when powdered substances are added to warm ether—a very risky procedure.

Ether will not mix with water, but when the two liquids are shaken up together a small quantity of the ether is dissolved in the water and *vice versa*. In the former case no risk of inflammability is communicated to the water, and in the other the dangerous character of the ether remains undiminished.

Ether does not ignite or explode spontaneously as a rule, though circumstances may arise under which it acquires a tendency to explode with violence. Prolonged exposure to air or direct sunlight results in partial decomposition of the ether, with formation of vinyl alcohol and hydrogen peroxide. When the ether is evaporated, these two products impart to the residual ether a by no means insignificant capacity of explosion, which may find manifestation at the vaporisation temperature (194° F.), or on percussion or violent shock.

Oxygen, ozone, and carriers of ozone, like oil of turpentine, induce in ether the formation of a highly explosive substance, ethyl peroxide, which may explode at 167° F., especially in presence of organic substances, fats, or oils. To guard against these, usually dangerous, explosions, it is advisable to replace ether by petroleum ether or benzol. Should this substitution be impracticable, care must be taken to preclude all conditions favouring the production of vinyl alcohol and hydrogen peroxide. For the foregoing reasons, therefore, ether should, in general, be sheltered from air, sunlight, oxygen, ozone, and carriers of the two latter substances.

Moreover, ether must not be brought into contact with per-acids (permanganic acid); otherwise it will take fire spontaneously.

Ether vapour, in small amount and out of contact with air, is not

dangerous. It may even be directed, as a thin stream, on to glowing platinum, without taking fire, though the incandescence of the platinum is maintained (analogous to the case of the formaldehyde lamp (*q.v.*) with the vapour of methyl alcohol). This behaviour forms the fundamental principle of the so-called eternal lamp, or platinum glow-lamp, for disinfecting sleeping rooms and sick chambers. In view of the small quantity of ether vapour liberated, there can be no question of danger unless the filled lamp be carelessly handled (see *Disinfection*).

On the other hand, when large volumes of ether vapours are liberated from heated open vessels, great danger is incurred owing to their ready inflammability and high explosibility on admixture with air. These vapours tend to migrate, and then give rise to the "ignition produced by remote fire," already mentioned under *Explosion*. The frequent explosions of ether vapour in places where no fire is present, must be ascribed to this migratory tendency of the vapour, as in the case of benzol and carbon disulphide.

Even a small quantity of ether vapour is sufficient to form an explosive mixture with air or oxygen; and the explosions are usually of an extremely violent nature. The danger is still further increased (in presence of vegetable or animal fibres) by a circumstance that is not always under control, namely, the formation of small electric sparks, which have always an injurious effect. Wherever two suitable metals are in contact, electric sparks may be produced, and even the faintest of these will ignite ether vapour, provided enough air be present.

Moreover, according to the experiments of Finzelberg, it is not even essential that two metals should be present, a simple metallic tube, continually traversed by ether, becoming thereby sufficiently electrified to generate small sparks. In the course of its varied applications, ether and its vapours frequently come in contact with metal and metallic fittings; hence the ignition and explosion of the vapour (in admixture with air) is a by no means rare occurrence, and one that is often attended with the gravest consequences.

Explosions of this kind are greatly furthered by the ether being maintained in rapid motion and brought into intimate contact with air. Owing to the absence of the necessary oxygen, an explosion of ether vapour by electric sparks is not easily effected in half-filled vessels wherein the ether vapour has completely displaced air, or in cases where the ether is quiescent. So much the greater is the danger of electrical ignition, when, in order to purify an article from fatty matter, it is plunged into ether, the latter and its vapours being thereby set in motion and enabling the air to gain access to the ethereal atmosphere.

This explains why explosions are rare in vessels for storing ether, except when work is in progress, the usual time for such explosions being soon after work has begun.

Ether vapours are more liable than any others to be ignited by electric sparks, next to them coming benzol and carbon disulphide vapour. In the case of alcohol the vapours require to be heated before they can be ignited or exploded by these sparks.

In using sulphuric acid in the production of ethereal preparations, the acid must not be poured into the ether (as in mixing this acid with water); but the ether must be added very slowly to the acid, otherwise the reaction will be extremely violent and explosive.

The preparation of ether is an exceedingly dangerous operation. A mixture of alcohol and concentrated sulphuric acid is distilled; and in proportion as ether distils over, more alcohol must be added. The operation is performed at a temperature of 284° F., which is generated by the heat of the reaction (spontaneous heat) and must be characterised as very high in view of the fact that ether boils at 95° F. An efficient cooling of the distillate, and an accurate control and supervision of the process and temperature, are highly essential precautions.

Great care is also necessary in the purification of the crude ether.

Ether being a very expensive material in works where large quantities are consumed, it is frequently recovered for use over again, the means adopted being distillation with steam. These establishments, which naturally present numerous risks, should be very carefully inspected and subjected to the same regulations as other dangerous works. Before accepting the insurance risk, it should be ascertained whether the recovery of the ether is practised, and if not, what becomes of the consumed ether or ether residues, and how they are rendered innocuous.

Ethyl acetate (*q.v.*) is employed as a substitute for ether, and is less dangerous to use.

It sometimes happens that, to save expense, impure commercial ether is purchased, and purified for use. The purification consists in distilling the impure ether, with 5–10 per cent. of liquid paraffin, at 105°–120° F. This operation is attended with the usual dangers of its class, especially towards the close of the distillation, at which stage the temperature is raised (often to 212° F.) in order to drive over the impurities remaining in the still and containing ether and other inflammable vapours.

The uses of ether are as multifarious as those of alcohol. Its chief employment is as a solvent for fats, oils, sulphur, phosphorus, bromine, iodine, sublimate, ferric chloride, gold chloride, resin, caoutchouc, ethereal oils, chloroform, acetone, camphor, organic acids, dye-stuffs;—and in the production of numerous preparations: collodion, lactic acid, tannin, ice, detergent solutions, cosmetic washes; and as a reagent in the laboratory, by apothecaries and in dairies.

Wherever ether is prepared or used, proper provision must be made for its safe storage, and that of the ethereal preparations, everything being avoided that might lead to ignition or explosion by the lighting or heating appliances.

Vessels containing ether should not be filled to more than eight-ninths of their total capacity, and must be kept closed and sheltered from the sun. Neither rubber nor canvas piping may be used for the conveyance of ether, the only admissible means being flexible metal pipes.

Ether fires in closed rooms must be extinguished by cutting off the supply of air by closing the ventilators, windows, and doors, or by means of steam or carbon dioxide. Water should, as far as possible, be avoided, since in running away it may carry the burning ether with it. When occurring out of doors, such fires should be extinguished by the aid of sand, earth, or ashes, a sufficient supply of these materials being kept at hand and in a dry condition.

If ether takes fire in the vessels, the latter must be covered or closed immediately, since burning ether is so rapidly vaporised by its own heat

that an explosion quickly ensues. Once closed, the vessels must not be reopened until the contents are *thoroughly* cooled down.

## 2. Compound Ethers

Ether combines with acids and forms a number of volatile, inflammable liquids the vapours of which are explosive when mixed with air. Some of these explode when merely heated rather quickly, whilst others liberate great heat at the moment of formation, so that (as in the case of ether itself) the process may entail great risk.

A few of these compound ethers are discussed below. It is necessary to mention that when the insurance of this class of compounds is in question, the exact description of the ethers should be given, some of them being safe whilst others are dangerous.

**Formic Ether** (rum essence, rum ether). Sp. gr. 0.917; boiling point 129° F. This ether is combustible, and its preparation is attended with danger on account of the great spontaneous heating that occurs during the mixing of the ingredients: sodium formate, alcohol and sulphuric acid. The product is largely used in the manufacture of rum and liqueurs.

If ethyl alcohol be replaced by methyl alcohol, the product will consist of methyl-formic ether, which boils at 96.8° F.

**Acetic Ether** (ether acetate, ether aceticus). Sp. gr. 0.905; b.p. 163.4° F. This combustible product is prepared in the same way as ether, from sodium acetate, alcohol and sulphuric acid. In point of danger it stands midway between ether and 98–99.5 per cent. alcohol. It is largely used where ordinary ether would be too dangerous.

**Nitric Ether** (ethyl nitrate). Sp. gr. 1.110; b.p. 185° F., combustible; explodes when rapidly heated; is formed when alcohol is mixed with nitric acid. The process is endangered by the concurrent formation of nitrous ether (*q.v.*), to prevent which an addition of urea is made to the mixture.

**Nitrous Ether** (ethyl nitrite, sweet spirit of nitre). Sp. gr. 0.947; b.p. 61 $\frac{3}{4}$ ° F. Very readily inflammable and combustible. Extremely dangerous owing to its tendency to spontaneous explosive decomposition during storage. It is prepared by passing nitrous acid gas through alcohol; both in this operation and the storage of the product, efficient cooling appliances must be provided, and the greatest care exercised. The temperature must never be allowed to exceed 50° F., or explosions may be expected.

On account of its high risk, it must be greatly diluted with alcohol for use. It is now largely employed in varnish works for dissolving resin; and it forms a source of danger in these establishments (see also *Pharmaceutical Chemists*).

**Methyl Nitrate**. Sp. gr. 1.182; b.p. 150 $\frac{3}{4}$ ° F. Formed by mixing together saltpetre, sulphuric acid, and methyl alcohol, the spontaneous heat disengaged being sufficient to distil the product. Efficient cooling must be provided. The substitution of ammonium nitrate for saltpetre is said to diminish the risk of explosion. The vapour explodes at 356° F., and the liquid on percussion or a violent blow.

**Methyl Nitrite**. This is a gas that is not met with in commerce.

When condensed to the liquid condition, it boils at 10° F. (−12° C.). Must be regarded as highly dangerous.

**Richardson's Ether** (ozonised ether). This is not a true ether, but merely a solution of hydrogen peroxide (*q.v.*) in ether, and has a greater fire risk than the last named.

Of the other organic matters the following may be noticed.

## CHAPTER LIII

### ACETONE, CHLOROFORM, CARBON DISULPHIDE

#### 1. Acetone (Dimethylketone)

Sp. gr. 0·814; b.p. 132 $\frac{3}{4}$ ° F.

In point of danger, this readily inflammable and combustible liquid is about on a par with benzol. Thus, if we represent the risks of ether by 100, those of pure benzol will be 99; methyl alcohol, 96; acetone, 97; alcohol (96 per cent.), 93.

Acetone is frequently met with in wood spirit, and is formed by the dry distillation of wood and of acetates (*q.v.*) as also in the manufacture of aniline, where it appears as a by-product when acetic acid vapours are heated to redness. It constitutes the most dangerous factor in highly heated acetic compounds.

When heated with hydrogen peroxide (see *Disinfection*), acetone produces highly explosive hydrogen trioxide.

Acetone has a high solvent power towards acetylene (*q.v.*).

It is frequently used in place of the more dangerous benzol for cleaning galvanised articles, in varnish-making (acetone lacquer), for dissolving resin, fat, oil, for purifying crude anthracene in the manufacture of dye-stuffs, and in the production of artificial silks.

In nearly all cases where acetone is used, large quantities (up to about 15 cwt.) are in question, and the recovery of the acetone is practised—an operation entailing the greatest care in view of the explosive and inflammable nature of the substance and its vapour.

In insurance cases, accurate information as to the process and methods of storage of the acetone must be furnished by the works.

#### 2. Chloroform (Trichloromethane)

Sp. gr. 1·500. Vapour density, 4·19. B.p. 141 $\frac{3}{4}$ ° F.

Chloroform will not burn without a wick, is a fairly safe liquid, difficult to ignite, and the vapours are not explosive.

On the other hand, the method of preparation is somewhat risky, bleaching powder being treated with alcohol, whereupon sufficient heat is spontaneously disengaged to distil the chloroform produced.

### 3. Carbon Disulphide (Alcohol sulphuris, Carboneum sulphuratum)

Sp. gr. 1.268; b.p. 113° F. (46° C.); melting point, -110° C.

Vapour density, 2.64; flashing point, -20° C.; solidification point, -116° C.; burning point, -20° C. (at which temperature it still vaporises); point of spontaneous ignition, 145° C., 149° C., 170° C. (293°, 300°, 338° F.).

This is a highly dangerous, colourless to pale yellow liquid, of high refractive power, and extremely inflammable, even at -20° C.

The greatest danger of this substance resides in the volatility of its inflammable vapours (which form explosive mixtures with air), and its liability to ignite spontaneously when heated to 293° F. (or 300°, 338° F., according to other observers).

On account of this great volatility, carbon disulphide must always be kept under water, by which it is dissolved to the extent of about 0.5 per cent., without any dangerous properties being thereby imparted to the water itself.

Owing to the great density of the vapours, the floorings of all rooms where it is employed must be well made, to prevent penetration by the vapour; and all depressions to which the vapour could gain access must be well covered (see *Explosions by Remote Fire*).

Where large quantities of carbon disulphide are employed, no fires should be allowed within 50 ft. of the workrooms.

Despite their volatility the vapours of carbon disulphide are tenaciously retained by porous, fibrous, woollen materials; and in the ground they are retained for more than a year.

By reason of this retentive faculty, carbon disulphide cannot be used for extracting fat from wool, though otherwise the best agent for that purpose. All porous materials treated with carbon disulphide remain dangerous for a considerable time from the above cause.

The great inflammability of carbon disulphide can be most clearly shown by dipping a warmed glass rod in ether, and then bringing it into contact with a little disulphide, whereupon the latter at once takes fire.

In itself, liquid carbon disulphide is not explosive, but the presence of even 6 per cent. of its vapour in air is sufficient to impart an explosive tendency to the latter. This tendency is retained in all cases where the proportion is higher; and therein lies the great danger of this substance (see *Gas Explosions*). The risk is increased when the air is replaced by oxygen, violent explosions occurring whatever the proportions of the mixture.

The vapours do not explode spontaneously except at high temperatures, though, according to Poepel, explosions are possible at 212° F., or even a few degrees lower; a favouring influence in this respect is exerted by contact with dusty metallic surfaces. Pipes containing steam under a pressure of about 3-4 atmos. (291°-305° F.) are stated to induce explosion in surrounding vapours of carbon disulphide, hence such pipes

should be enclosed in insulating materials if they cannot be removed altogether.

Rooms containing carbon disulphide must not be heated or visited with open fires or lights. Even safety lamps are unsuitable for use in this case, and in fact the only permissible method of lighting is by electric incandescent lamps in protected bulbs.

All vessels containing carbon disulphide must be sheltered from the sun and from the influence of any glass articles that may act the part of reflectors or lenses. Considerable protection in this respect is afforded by a fairly thick stratum of water above the carbon disulphide, which is thereby prevented from vaporising.

The preparation of carbon disulphide, by passing sulphur vapour over glowing charcoal in iron retorts, is a process by no means free from danger, particularly at the stage of purifying the crude product by distillation.

The following rules should be followed in this process, whether on a large or small scale: large open rooms with copious ventilation; thorough cooling of the carbon disulphide vapours; all taps, valves, and pipe orifices must be situated as far away from the fire as possible; the steam pressure in the pipes and apparatus must not exceed 2 atmos.; and wherever carbon disulphide is used, care must be taken to prevent the vapour being subjected to pressure, since under these circumstances the danger of explosion is greatly augmented.

A highly important point in connection with carbon disulphide is the loss occasioned by leaky fittings, &c., sometimes amounting to  $\frac{1}{2}$  per cent.; in fact, a loss of about 10 lbs. of the disulphide out of every ton of this substance used is inevitable even with the most perfect forms of apparatus. On this account and because in rooms of moderate dimensions this quantity is sufficient to render the air explosive, it is necessary to provide ventilation of a most thorough character. Insurers should attach no credence to statements that the apparatus is perfectly vapour tight.

The vicinity of railways or other sources of sparks constitutes a standing menace to carbon disulphide plant; and the risk is only increased by the provision of ventilating towers in the roof.

Carbon disulphide is a difficult substance to store. In the case of metallic storage vessels, there is the inconvenient fact that the metal is corroded by the contents, metallic sulphides being formed, particularly with iron vessels, which thus become coated with an internal lining of iron sulphide. This substance has proved a source of special danger, instances having been known where iron pipes conveying carbon disulphide have given rise to explosions when hammered to remove the incrustation. Iron sulphide is also spontaneously explosive under certain conditions, especially when exposed to the air in the state of finely divided dust (see *Metallic Sulphides*).

Hence iron should be avoided as far as possible, and all vessels and pipes be constructed of copper or zinc, since these metals, although attacked by the disulphide and encrusted with the corresponding sulphur compounds, do not form explosive products.

Glass is the best material for storage vessels, but its application is limited in view of its fragility and of the large dimensions generally required.

The pipes for conveying carbon disulphide should be as short and free from joints as possible, and made of copper or glass. Rubber pipes must not on any account be used, being quickly destroyed by the solvent action of the disulphide. This applies also to other organic substances used in making pipes, no permanent protection being afforded even by the usual linings employed.

From the generally dangerous character of carbon disulphide, it might be expected to furnish numerous highly dangerous and explosive compounds. This, however, is not the case, for, with the exception of iron sulphide, its behaviour towards other substances is innocuous. In admixture with certain bodies, however, it forms a source of danger; for instance, with per-acids, permanganic acid, permanganates, and carriers of oxygen or ozone it becomes readily inflammable. With metallic potassium or sodium it forms a brown substance, which explodes violently under pressure or friction. The mixtures with hyponitrous acid (panclastite) are highly explosive, but not by shock or friction, only at 200° C. and by the action of mercury fulminate or gunpowder.

On the other hand, attempts have been successfully made to convert carbon disulphide into a harmless form without loss of certain of its useful properties. Thus, when carbon disulphide is mixed with alkali sulpholeates, which dissolve it to the extent of 40–50 per cent., a harmless product known as "polysolve" is obtained. This substance is soluble in water and thus furnishes an innocuous dilute solution of the disulphide, unobjectionable as a disinfectant or insecticide.

Attempts to replace carbon disulphide by other and safer substances have not been wholly successful. Where it is a question of extracting fats or oils from substances prone to rancidity, seeds, fruits, cleaning waste, &c., or of recovering sulphur from industrial waste products (spent gas-lime, &c.), carbon disulphide cannot be replaced, and it is also unapproachable as a solvent for resinous substances.

Where, however, less powerful solvents will do, the disulphide can be superseded by other materials, *e.g.* ether, benzol, or petroleum ether, which, though not much safer than the disulphide, possess the advantage of being far more readily expelled from the extraction residues than is the case with the disulphide.

On the other hand, carbon tetrachloride forms a perfectly harmless substitute for the disulphide. This substance has the sp. gr. 1.600, boils at 170½° F., furnishes inexplodable vapours, and can be recovered, when contaminated by use, by a fairly safe process of distillation (see *Benzol*).

Carbon disulphide is employed—for the most part in considerable quantities—in numerous industries, *e.g.* those dealing with caoutchouc, rubber, oil, fat, resin, ethereal oils, waste products (gas-lime, bone fat), sulphur, potassium ferrocyanide, paper, kindling materials, cellulose, blasting explosives, electro-plating, dye-stuffs, preservatives, disinfection, lighting, ice-making, physical instruments, phosphorus, and camphor.

All establishments of the above kind should be subjected to regulations of a most stringent character, special danger attaching to solutions of phosphorus in carbon disulphide, and the employment of the disulphide as a vermin killer or in the preparation of explosives for blasting.

Carbon disulphide fires are quite as dangerous as those of benzol, and explosions are liable to occur. In closed rooms, on the other hand, burning carbon disulphide can be extinguished by the products of its

own combustion (sulphur dioxide), unless the storage vessel should prematurely explode or carriers of oxygen be present (in which latter event an explosion may be produced). Under certain circumstances water may be used in extinguishing these fires, being specifically lighter than the disulphide, though it must not be applied in such a manner as to carry off any of the burning liquid, since this would merely spread the fire. Where the conditions seem to justify the use of water, large quantities of the latter must be employed. In other respects these fires resemble those produced by benzol (*q.v.*), and must be dealt with in the same manner.

# PART X — DANGERS PRODUCED BY METALS, OXIDES, ACIDS, OR SALTS

## CHAPTER LIV

### METALS

#### 1. Metals, Heat, and Water

IN daily life the term “metallic” or “of metal” is regarded as synonymous with incombustibility; but though this is true of some metals and under certain conditions, in a far greater number of instances metals prove combustible and even inflammable, liable to spontaneous ignition, the cause of dangerous explosions, and quite unreliable in fire, even when in compact masses.

Of the two chief classes into which metals are divided, light and heavy metals, the former generally exhibit the greater fire risk. This does not imply that the heavy metals are free from very serious risks, since in certain states and under certain circumstances the latter often exhibit great dangers.

Metals are dangerous when :

1. They are themselves combustible.
2. They are in an extremely fine state of division.
3. They are capable of decomposing water into its component gases, oxygen and hydrogen, whether at ordinary temperature or at red heat.
4. When they dissolve in dilute acids and liberate hydrogen.

Most metals are combustible, *i.e.* can be ignited in air, and that too under the following conditions :

Potassium, sodium, rubidium, caesium, and lithium (at 200° C.) when gently warmed in air.

Calcium, strontium } when rather more strongly heated, *e.g.* by a  
Magnesium . . . } lighted match.

Aluminium, in the form of powder or wire, is easily ignited.

Uranium, in powder, ignites at 270° C.

Iron, in powder, will ignite spontaneously when freshly prepared.

Zinc, in powder takes fire when heated to 360° C.

Tin, when raised to white heat (1300° C.).

Bismuth, titanium . . . }  
Cadmium, molybdenum } on being strongly heated, even to near red  
Antimony, indium . . . } heat, when in the form of fine powder.  
Tungsten . . . . . }

Cobalt . . . . . } when raised to white heat (1300° C.), or  
spontaneously when in a fine state of  
division.

Nickel, manganese . . . .	} cannot be characterised as susceptible to ignition in air.
Chromium, lead, platinum . . .	
Gold, silver, mercury . . . .	

The metals most readily ignited in air, and therefore specially dangerous, are potassium, sodium, magnesium, aluminium, iron, and cobalt.

The other ignitable metals offer little danger in combustion, the operation being very brief and only possible under very favourable conditions; besides, the flame given out is small, and does not spread unless it be communicated to adjoining inflammable objects.

Greater dangers result from the contact of metals with water, owing to the formation of explosive oxyhydrogen gas or hydrogen, and the risk of spontaneous ignition of these products.

Water consists of two gases, oxygen and hydrogen, in a state of chemical combination; whereas, when merely mixed together, these two gases constitute highly explosive oxyhydrogen gas (*q.v.*).

Whilst oxygen is incombustible, though it supports and fosters the combustion of other substances and raises the flame and combustion temperatures, hydrogen is readily inflammable and exceedingly explosive when mixed with air or oxygen.

When certain metals, or metals under certain conditions, are placed in contact with water, their tendency to combine with oxygen is so great as to decompose the water, the metal combining with the oxygen and liberating the hydrogen. Sometimes the act of combination is attended with the generation of sufficient heat to ignite the hydrogen, or, when in admixture with air (oxyhydrogen gas), cause it to violently explode.

The following table shows the behaviour of various metals towards water, the latter being decomposed by (see also *Amalgams*):

#### 1. *Water at any Temperature.*

Potassium . . . . .	The liberated hydrogen ignites at once explosively.
Rubidium . . . . .	Ditto.
Sodium . . . . .	Ditto, but less easily.
Lithium . . . . .	No ignition.
Caesium . . . . .	„
Calcium . . . . .	„
Barium . . . . .	„
Strontium . . . . .	„

These metals should *never* be brought in contact with water, aqueous solutions, damp bodies, fog, or steam.

#### 2. *When the Water is Warm.*

Magnesium . . . . .	Slight decomposition at 30° C., strong at 100° C.
Zinc . . . . .	Decomposition at 100° C.
Cadmium . . . . .	Slight decomposition only.
Manganese . . . . .	Exceedingly slight (see 3).
Titanium . . . . .	Decomposition at 100° C.
Uranium . . . . .	Decomposition extremely slow.

These metals should *never* come in contact with hot water or hot aqueous materials.

3. *When the Metal is in a finely divided state.*

Manganese . . . .	Strong decomposition (see 2).
Aluminium . . . .	Slight, but strong with warm water.
Zinc . . . . .	Dangerous with zinc dust.

These metals should never be put in contact with water, &c., while in powder form.

4. *When the Metal is Glowing.*

Iron . . . . .	Strong decomposition, often explosive.
Cobalt.	
Copper . . . . .	Only slight, at white heat.
Nickel . . . . .	Only slight.
Bismuth.	
Tin.	
Antimony }	Behave like the elements of this group.
Boron . . }	

These metals should never come in contact with water, damp bodies, &c., whilst glowing.

The light metal, gallium, behaves like sodium (see 1), when combined with aluminium.

Certain metals also produce hydrogen or oxyhydrogen gas with acids, as well as with water. To this category belong all the metals specified under 1 and 2 of the foregoing list, and also :

Iron	with hydrochloric acid or sulphuric acid.	
Zinc	"	"
Indium	"	"
Nickel	"	"
Cobalt	"	"
Manganese	"	"
Chromium	"	"
Uranium	"	"
Tin	"	"
Aluminium	"	and also with caustic soda or potash.
Gallium	"	" "
Titanium, zirconium	"	" "
Copper	"	in presence of platinum.
Like aluminium and gallium, the following give hydrogen gas :		
Vanadium	with fused caustic potash.	
Tin	" caustic potash.	
Tungsten dioxide	" hot caustic potash.	

The following metals are inert, or at least give off no explosive hydrogen gas, in presence of either of the foregoing acids :

Lead, mercury, silver, gold, and platinum.

2. **Alloys and Amalgams**

A combination of two or more metals is termed an alloy, but where one of the ingredients consists of mercury, the product is called an

amalgam. A further difference between the two is that alloys are formed only at high temperatures, whereas amalgams can be obtained at the ordinary temperature.

The metals exhibiting a special tendency to combine with mercury and form amalgams are: Potassium, sodium, magnesium, zinc, lead, aluminium, bismuth, silver, and gold.

All amalgams containing metals capable of decomposing water retain this property also, under the same conditions, and therefore, on account of the risk of producing explosive hydrogen, must be protected from contact with wet or moisture.

The formation of potassium or sodium amalgam is accompanied by the production of flame, and therefore capable of exciting ignition.

In most cases where amalgamation is to be practised (usually on objects of metal or glass), strong heat is required, *e.g.* 230°–260° C. in the case of zinc; other metals up to red heat, 400°–500° C. For the formation of alloys a heat equal to the fusion temperature of the component metals is required, the usual practice being to fuse the most refractory and add the other to it. In some cases, instead of working direct with the metals, their oxides are raised to high temperatures in presence of charcoal. This operation is attended with violent flaming, and needs a perfectly fireproof plant, such as a foundry or the like.

The heat liberated is particularly great in the case of tin and platinum; and considerable spontaneous accessions of temperature ensue on the addition of the second metal. For instance, if platinum be added to antimony, which fuses at 430° C., the mass immediately becomes red hot spontaneously.

The fusing points of alloys are generally lower than those of the component metals. Whereas lead fuses at 327° C., bismuth at 271° C., and tin at 227° C., their alloys will melt at as low as 98° C., *i.e.* in boiling water.

Alloys are occasionally explosive (see *Explosions*). The only alloy at present known capable of decomposing water, with the formation of explosive oxyhydrogen gas, is that of gallium and aluminium, which acts as powerfully as metallic sodium.

### 3. Various Metals and their Dangerous Compounds

(a) **Potassium and Sodium** (see foregoing table). These two light metals are very similar, potassium being the more dangerous. Their affinity for oxygen is considerable, and they decompose water at the ordinary temperature, the liberated hydrogen taking fire spontaneously. They must be well protected from water or moisture, and always stored under petroleum or other liquid free from oxygen. Even petroleum is not universally safe as a protective medium, since some kinds of this oil contain oxygen; and very violent explosions have been known to result from this cause. Preference should therefore be given to the far safer, oxygen-free vaseline oil.

Low temperature and careful handling are requisite when dealing with either of these metals, since they will ignite in the air if gently warmed. Should an outbreak of fire occur in any place where these metals are stored in quantity, water must not be used for quenching.

The metals are prepared at white heat (1300° C.) from their respective

carbonates, *i.e.* potash for potassium, and soda for sodium. The process furnishes the dangerous products, explosive potassium carbon monoxide, and combustible carbon monoxide gas, which latter may also form explosive mixtures with air.

The metals are sold in lump form, under fancy names, for Will-o'-the-Wisp lights, and then constitute dangerous playthings, igniting and exploding when thrown into water.

The following are the more dangerous compounds of these metals from the fire insurance point of view.

Potassium hydride, which is formed at  $390^{\circ}$ – $570^{\circ}$  F., and ignites spontaneously.

Potassium chlorate is highly explosive (see *Chlorates*).

Potassium nitrate (nitre, saltpetre), detonates easily. Textiles and fibres impregnated with this salt take fire on the slightest inducement (see *Chili Bags*), a small spark, or even sulphuric acid (see *Nitration*), being sufficient.

Potassium peroxide readily parts with its oxygen, and, like the corresponding sodium compound, is explosive.

Potassium picrate is explosive (see *Picric Acid*).

Sodium peroxide is formed at  $750^{\circ}$  F., by heating metallic sodium. When treated with water, it liberates a quantity of oxygen, and therefore favours the spread of flame; it is explosive.

Sodium nitrate (see *Nitrate of Soda*).

Sodium carbide begins to glow spontaneously when introduced into carbon dioxide, sulphur dioxide, or chlorine gas; it explodes on contact with water or bromine.

Sodium picrate (see *Potassium Picrate*).

Potassium and sodium cyanide (see *Hydrocyanic Acid*).

Sodium nitrite explodes with ammonia salts or potassium cyanide at  $400^{\circ}$  C.

(b) **Calcium.** Metallic calcium decomposes water, but ignites when more strongly heated. Is prepared by electrolysis at dull red heat ( $700^{\circ}$  C.).

The metal itself is not much used; on the other hand, its oxide, known as quick or burnt lime, finds extensive employment.

The burning of limestone (calcium carbonate) to quicklime, or of gypsum (calcium sulphate) to plaster of Paris, is not free from risk, in the event of the kiln flues getting choked so that the furnace gases cannot escape properly (see *Stove Explosions*).

The most dangerous calcium compounds are:

Calcium nitride: ignites spontaneously in air; energetically decomposes water.

Calcium carbide (see *Carbide*).

Calcium silicide: liberates hydrogen from water.

"Chloride of lime" (Calcium hypochlorite, bleaching powder): liberates oxygen so energetically when exposed to heat or the sun that the reaction may attain an explosive character, and sometimes bursts the vessel. If impure chlorine (containing hydrogen) be used in the preparation, violent explosions may result from the formation of mixtures of hydrogen and chlorine, which explode in the sun.

Calcium sulphide is dangerous from its tendency to spontaneous ignition (see *Metallic Sulphides*).

Quicklime (lime burned at  $600^{\circ}$ – $900^{\circ}$  C.), agricultural lime (see *Manures*). The affinity of quicklime for water (and also for acids) is so strong that the combination is attended with considerable generation of heat, the water often boiling. The greatest heat is evolved when the lime is mixed with one-third of its own weight of water, the temperature then attaining  $150^{\circ}$  C. ( $302^{\circ}$  F.) when the amount of lime is small; but when large heaps of lime are in question, and the accumulation of heat is thereby facilitated, the temperature may easily rise to  $300^{\circ}$  C. ( $570^{\circ}$  F.), and indeed reach such a height as to set fire to adjacent inflammable substances like straw, paper, chips, boards, &c. Under extremely favourable circumstances, temperatures as high as  $600^{\circ}$ – $800^{\circ}$  C. have been observed in practice, in which event the lime becomes incandescent.

Hence, though lime is not in itself combustible, it may in this way engender spontaneous ignition.

When lime has combined with water, *i.e.* become "slaked," all its dangerous characteristics disappear, milk of lime, for instance, being perfectly innocuous.

Quicklime must be stored in fireproof rooms, with dry flooring, and protected from the rain. Should there be the slightest possibility of damp, the usual practice of covering burnt lime with straw, cloths, or boards is extremely dangerous, these substances readily taking fire. Experience has also shown that a certain amount of risk attaches to the use of quicklime for disinfecting purposes, inasmuch as it will set fire to substances containing carbolic acid, and itself become incandescent (see *Disinfection*).

Quicklime finds a large variety of uses: for building, in chemical industries (organic acids, caustic potash, ammonia, bleaching powder, gas works, soap, sugar, tanning, dyeing, grape sugar), for disinfection, as a preservative, for polishing, cementing, and also in the preparation of blasting explosives.

Gypsum is burned at far lower temperatures:  $120^{\circ}$ – $170^{\circ}$  C. ( $250^{\circ}$ – $340^{\circ}$  F.). Explosions are less likely to happen, though by no means entirely precluded should the kiln temperature be raised to  $500^{\circ}$  C. for the production of hydraulic plaster, and the kiln itself be defective or badly managed.

(c) **Aluminium**, fuses at  $660^{\circ}$ – $700^{\circ}$  C., boils above white heat. In compact masses, aluminium is perfectly harmless, but is easily ignited when drawn out as fine wire or in the form of small scales, and is even explosive when ground to fine powder. Any simple flame will set fire to aluminium dust. On combustion the metal furnishes a very high temperature, the heat of combustion being 7130 cal., or only a little inferior to that of carbon (8080 cal.) (see *Bronze Powders*).

When mixed with carriers of oxygen (see *Flash Powders*) it explodes by percussion.

In the compact state, the metal does not decompose water, though it will do so when finely powdered or mixed with caustic potash or soda, dangerous hydrogen being liberated. Aluminium amalgam behaves in a similar manner, the heat generated being occasionally so great that any ether, petroleum ether, benzol, or analogous substances present may be raised to ignition.

The decomposition of water also ensues when the same is in admixture with alcohol or glycerin, or is acting as a solvent.

The preparation of aluminium necessitates the high temperatures of the electric furnace (2800°–3000° C.).

Before fusing, aluminium is often dipped in petroleum or oil, and benzol is used for cleaning the metal; these agents increase the danger of the operations.

On the use of aluminium in generating high temperatures, see Goldschmidt's process; as a substitute for the dearer magnesium in flash-light preparations, see *Flashlights*; and for bronze-making, see *Bronze Powders*.

In all cases where the manipulation of explosive materials is in question, *e.g.* making fireworks, Bengal lights, blasting explosives, nitro-compounds, &c., and where there is a risk of igniting sparks being produced, the employment of aluminium as working material is advisable, since this metal does not generate sparks under shocks, percussion, or friction. It is equally suitable for vessels or apparatus in which the vapours of readily inflammable liquids might be exploded by the presence of sparks.

The following aluminium compounds are dangerous:—

*Aluminium triethyl*.—The preparation necessitates high temperature and pressure. When mixed with water it decomposes in an explosive manner, ethane being formed. It ignites spontaneously in air.

*Aluminium trimethyl*, ignites spontaneously as soon as exposed to the air; with water it immediately forms methane.

*Aluminium tripropyl*, a liquid that ignites spontaneously in air.

For alum, see later.

(d) **Magnesium**, fuses at 700°–800° C. Like aluminium, this metal is harmless in the mass, but easily ignited when in the form of wire or fine powder. It decomposes water, but only towards 100° C.

Its preparation requires the high temperature of the electric furnace, only in this case it is necessary also to employ hydrogen, or generator gas, to protect the still glowing metal from the influence of air and consequent combustion. This augments the danger of the operation.

The compounds, magnesium ethyl and magnesium methyl, take fire spontaneously in air, and, when brought into contact with water, furnish the combustible gases, methane and ethane.

Both compounds are also noteworthy from their faculty of burning in an atmosphere of carbon dioxide, which usually extinguishes all combustion.

(e) **Tin**, fuses at 233° C. (451.4° F.), and requires for its preparation the heat of the reverberatory furnace; burns first at white heat, and decomposes water only when in the incandescent state. In other respects it is free from the risks exhibited by aluminium and magnesium.

Only one of its compounds, the protoxide (stannous oxide), is attended with the risk of ignition when gently warmed.

(f) **Bismuth**, fuses at 268° C., boils at 1700° C. It is recoverable at the temperature of the roasting furnace, and the greater heat of the reducing furnace. Innocuous in all forms.

Bismuth pentoxide (bismuthic anhydride) behaves as a carrier of oxygen. Bismuth triethyl is almost spontaneously ignitable, and explodes at 150° C. (302° F.).

Bismuth ethylchloride is a powder that takes fire spontaneously in air.

(g) **Antimony**, fuses at 430° C. Antimony decomposes water first at

red heat, and does not burn until very strongly calcined. It is prepared in the reverberatory furnace at red heat, and at still higher reducing heat.

Antimony trimethyl (trimethylstibine) is a liquid that ignites spontaneously in air; and the same applies also to antimony triethyl (triethylstibine).

(h) **Mercury.**—A low roasting heat, and a distillation temperature of  $358^{\circ}\text{C.}$ , are all that are required for the preparation of this metal. In itself the metal is quite harmless, but furnishes very dangerous compounds.

With nitrogen it forms mercury nitride (trimercuramine), a powder strongly explosive by heat, shock, or friction; the same applies also to dimercuric ammonium oxide.

With fulminic acid it forms the highly explosive mercury fulminate (see *Fulminates*).

(i) **Zinc**, fuses at  $412^{\circ}\text{C.}$ , boils at  $950^{\circ}\text{C.}$  It is prepared by roasting and distillation at  $1000^{\circ}\text{C.}$

In the form of powder (zinc dust), it commences to burn at  $360^{\circ}\text{C.}$  Though not pyrophoric like iron powder, it is very susceptible to moisture, *i.e.* decomposes water at the ordinary temperature, with liberation of hydrogen; when in the compact form, it does not decompose water below the boiling point of that liquid.

All stocks of zinc dust must be well packed, and protected from all dampness produced by water or fog. The decomposition of water is accompanied with the liberation of sufficient heat to ignite the hydrogen evolved. This reaction may set fire to stores of zinc dust, a phenomenon that was formerly highly puzzling (oxyhydrogen gas).

All vessels containing zinc dust, must be marked "to be kept dry." Greater danger is incurred when zinc dust is exposed to the action of even the most dilute of acids, the liberation of hydrogen being then of an explosive character and mostly culminating in violent, fiery explosions.

Zinc is rich in dangerous compounds. The preparation of those mentioned below must be effected solely in an atmosphere of carbon dioxide (which prevents combustion, except that of certain magnesium compounds, *q.v.*); and the operation is specially dangerous on account of the relatively high temperatures ( $130^{\circ}$ – $150^{\circ}\text{C.}$ ) required.

Zinc methyl	boils at $46^{\circ}\text{C.}$ ( $114.8^{\circ}\text{F.}$ )	} All these compounds are liquids that ignite spontaneously in air, and liberate inflammable gases, like ethane, methane, &c. when mixed with water.
Zinc ethyl	„ $118^{\circ}\text{C.}$ ( $244.4^{\circ}\text{F.}$ )	
Zinc propyl	„ $150^{\circ}\text{C.}$ ( $302^{\circ}\text{F.}$ )	
Zinc isobutyl	„ $168^{\circ}\text{C.}$ ( $334.4^{\circ}\text{F.}$ )	
Zinc isoamyl	„ $220^{\circ}\text{C.}$ ( $428^{\circ}\text{F.}$ )	

Zinc chloride is not of itself dangerous, but its preparation on the large scale easily gives rise to violent explosions of oxyhydrogen gas (*q.v.*).

(k) **Iron.**—Iron behaves in different ways, according to its carbon content: with 2.3–5 per cent. of carbon it constitutes: 1. pig or cast iron, which may be:

1. Grey pig iron, melting at  $1050^{\circ}$ – $1300^{\circ}\text{C.}$
2. White pig iron, melting at  $1050^{\circ}$ – $1300^{\circ}\text{C.}$
3. Spiegeleisen, with 5–20 per cent. of manganese.

## 4. Mottled pig iron.

With less than 2.3 per cent. of carbon: II. forgeable iron, which may be:

1. Steel, with 0.5–2.3 per cent. of carbon, melting at 1300°–1800° C. and furnishing:

(a) Ingot steel (Bessemer-Martin steel), when prepared in a molten state, or

(b) Welded steel (puddled steel), when prepared by welding.

2. Wrought iron, with 0.4–0.5 per cent. of carbon, melting at 1800°–2200° C., and furnishing:

(a) Ingot iron (Bessemer-Martin iron), when molten, or

(b) Welded iron (puddled iron), when obtained by welding.

Iron is prepared at very high temperatures, in large blast-furnaces, which are exposed to great dangers (see *Furnace Explosions*).

In the form of fine powder, iron is pyrophoric, *i.e.* ignites spontaneously when fresh. Analogous finely divided iron is obtained by reducing ferric oxide (iron rust) in a current of hydrogen at low red heat, and also by calcining iron tartrate, oxalate, nitrate, or malate in a closed vessel. When this finely divided iron is exposed to the air, it endeavours to combine with the atmospheric oxygen, and thereby generates a temperature of 525°–700° C. and ignites.

This tendency to spontaneous ignition vanishes when the iron powder is cooled down very gradually and completely before exposure to the air (like fresh charcoal).

Finely divided iron, *e.g.* turnings, is also liable to take fire spontaneously when piled in large heaps, and exposed to moisture and desiccation. Heaps of turnings, accumulated as waste in the yards of metal works, have often been discovered in a glowing state; in one instance a fire of this kind was produced by a flood. Ignition is facilitated by the presence of residues of oil and soap adhering to these waste products.

Glowing iron must not be sprinkled with water, since the latter is thereby decomposed and liberates explosive oxyhydrogen gas. The following compounds of iron are dangerous:

Iron sulphide (see *Metallic Sulphides*), which when fresh is quite as pyrophoric as iron powder (see *Coal*). All cast iron articles that have lain for a long time in putrefying, sulphuretted water, exhibit a high tendency to glow spontaneously, the surface of the metal having become coated with a layer of iron sulphide that is so porous as to greedily absorb oxygen on exposure to air, and thereby generates sufficient heat to raise the entire mass to incandescence. This was observed in the case of an old cannon ball taken from the Rhine.

Iron carbide (see *Carbide*) takes fire at 150° C. (302° F.), and may, under certain circumstances, become pyrophoric. Compounds of ferrous oxide and tannin induce spontaneous ignition in silk (*q.v.*).

The hardening of iron, in the manufacture of tools, is not unattended with danger. The work should be carried on in fireproof premises, and no inflammable substances may be stored or worked near by.

The danger consists in that the tool or metal to be hardened is raised to cherry red heat (850° C.) and then dipped in the hardening material, which mostly consists of a fat, oil, or petroleum, either alone or in admixture with potassium ferrocyanide, borax, common salt, sugar,

ammonia, glycerin, powdered horn, glue, or saltpetre. Those containing petroleum or saltpetre are particularly dangerous, owing to the imminent risk of detonation or even explosion.

In hardening with oil or fat, a large supply of cooling water is essential to success, and in order that the hardening medium may be effectually cooled immediately after the immersion of the iron. The contact with the hot metal raises the temperature of the medium, and if the operation be repeated many times, the oil or fat may become sufficiently heated to disengage explosive vapours, which may then be ignited by contact with the glowing metal. It is greatly to the advantage of the tool manufacturer to keep the hardening medium as cool as possible, since on this the success of the operation depends. Such a course would diminish the risk of fires that are often of a violent character owing to the large quantities of oil involved.

For these reasons, the heating furnace and the oil tank should not be so close together that the latter may possibly be endangered by the fire of the former.

For the extinction of fire a sufficient store of dry sand, earth, or ashes should be kept near at hand; or at any rate the oil tank should be provided with tight-fitting covers. These precautions are all the more necessary because the entire hardening process is conducted in darkened rooms, to enable the degree of glowing heat to be under better observation; and in dark rooms the danger of fire is always greater than in such as are well lighted.

Latterly electricity has also been applied to the hardening process, the temperatures thereby attained being even higher than with the oil method, viz.  $860^{\circ}$ – $960^{\circ}$  C.

(*l*) **Lead**, fuses at  $325^{\circ}$  C., boils at  $1600^{\circ}$  C. This metal is prepared in the reverberatory furnace, and, under certain conditions, the process is accompanied by the formation of iron sulphide (see *Iron, Charcoal*). Lead is a perfectly safe metal, and though violent explosions have been known to occur during the re-melting of old scrap lead, these were due, not to the metal, but to gunpowder remaining adherent to the scrap metal. An explosion of this character, in which five tons of lead were concerned, took place at the Corvilain foundry, Paris, in 1889.

Some of the compounds of lead are highly dangerous. For instance, lead peroxide (see *Carriers of Oxygen*), must not be triturated with sulphur, or the latter will ignite; nor with phosphorus, or an explosion will ensue; nor may it be treated with sulphur dioxide, since it glows spontaneously in this gas.

Lead picrate may give rise to spontaneous ignition in textiles, silk in particular. Lead chlorite explodes at  $212^{\circ}$  F., and ignites spontaneously in presence of sulphur or metallic sulphides, the mixture exploding when rubbed hard. Lead triethyl explodes with iodine or bromine.

Red lead, or minium, has been known to produce a violent explosion when mixed with the dyestuff, eosine, and atomised in the form of dust, at a distance of five feet from a naked flame.

(*m*) **Copper**, fuses at  $1080^{\circ}$  C. Copper, like lead, is a perfectly safe metal, and only exerts a feeble decomposing action on water, even when white hot. It is prepared in roasting and reverberatory furnaces, at high temperatures.

Copper furnishes bronzes (see *Bronze Powders*).

It combines with acetylene, the resulting compound, of which very little is known, being highly explosive (see *Acetylene*).

(n) **Silver**, fuses at 954° C. Silver is harmless, but, on the other hand, it furnishes the extremely dangerous and explosive compound, silver fulminate (see *Fulminates*), when freshly prepared silver oxide is treated with ammonia.

Silver oxalate explodes somewhat violently when rapidly heated.

Silver nitrate furnishes silver fulminate when treated with alcohol, the mixture being highly dangerous.

Silver nitride (azide) is very explosive under percussion or when heated.

(o) **Gold**, fuses at 1060° C. This metal behaves like silver; and the same applies to its compounds.

Gold carbide explodes under percussion, friction, or rapid heating.

(p) **Platinum**.—When in the compact state, this metal is entirely innocuous; but when in a finely divided condition (spongy platinum, platinum black) constitutes a source of danger by its property of occluding gases by surface attraction, in virtue of which it is able to take up 100 times its own volume of oxygen, and 300 volumes of hydrogen. When such gas-laden platinum is immersed in an atmosphere of some other gas, combination between the two is greatly facilitated by the condensed state of the first gas, so much heat being evolved by the reaction that the platinum glows and the gases are ignited (Dobereiner's Gas Lighter). With ammonia, platinum furnishes the explosive platinum fulminate.

#### 4. Bronze Powders

The term "bronze" is generally understood to imply an alloy of copper and tin, which, when pulverised, furnishes bronze powder. Nevertheless, monometallic bronze powders, *e.g.* aluminium bronze, are also known.

When metals or their alloys are converted from the compact form into the state of nearly impalpable powder, they lose their incombustibility and power of resisting fire, and become readily ignitable. The enormously increased superficial area enables oxygen and also water to act upon them with far greater energy, and oxidation proceeds so violently that it becomes necessary to protect the bronze from such risk by the admixture of some fatty substance. A very small quantity is sufficient for this purpose, about 1 oz. of purest olive oil being enough for 20 lbs. of bronze powder.

In estimating the risks caused by bronze powders, a distinction must be drawn between the storage, preparation, and use of the material.

When packed and stored perfectly dry and well protected from damp vapours, finished bronze powder is quite free from risk, no matter whether it was made from alloys (copper, tin, brass), or from single metals (aluminium). In addition it is essential that the wrapping or packing materials should not contain gum, glue, acids, or meal, likely to render them hygroscopic, or cause the liberation of acid vapours; and they must also be free from any carriers of oxygen.

The presence of this latter class of substances renders bronze powders

liable to explode, whilst moisture induces the formation of hydrogen (oxyhydrogen gas). A single pound of bronze powder will liberate as much as 42 cubic feet of hydrogen; and a little more than a hundred-weight of the powder will suffice to fill a fair-sized room with this gas. Indeed, a far smaller quantity is necessary to produce an explosive mixture of gas and air, about 14 lbs. being enough for this purpose. In presence of considerable moisture, or in direct contact with water, the liberation of gas is so violent as to be explosive, and is accompanied by ignition, the violence of the explosion being intensified by the presence of an acid or heat.

As already mentioned, the contact of bronze powders with carriers of oxygen is attended with a high explosion risk, the powder acquiring the properties of a charge of blasting explosives; an actual explosion only occurs, however, when induced by some external influence (percussion, shock, violent friction, flame, sparks, heat, moisture).

Bronze powders must be stored in a cool place; and, as they are liable to heat spontaneously up to a temperature of 150° F. when merely slightly damp (air), the storerooms must never be warmer than 68° F., the walls and flooring being kept dry, and the dissemination of moisture prevented.

The finer the powder the greater the risk, the maximum being reached when the powder floats in the air as dust. This may occur during the use or preparation of the powder, in polishing mills, sifting, &c., the fine powder floating in regular clouds of dust. In such cases the presence of the smallest amount of moisture is highly dangerous. The powder must be introduced in a perfectly dry state, and be kept warm enough to prevent any deposition of moisture thereon in the warmer atmosphere of the mills; otherwise the liberation of explosive hydrogen (oxyhydrogen gas) will ensue.

The temperature in polishing mills usually averages about 98° F., or at least may easily rise to this degree; and the bronze powder must be warmed to about the same temperature if the deposition of moisture is to be prevented.

The bronze powder floating about in the sifting mills (aluminium bronze in particular) does not explode on percussion, shock, or friction, though it will do so on contact with a flame or spark (metallic dust explosion). Consequently the mills must be so arranged as to render the production of sparks an impossibility, the lighting of the interior with naked lights being also prohibited. These dust explosions are, as a rule, not much less powerful than those of flour.

The following regulations should be laid down:—

All mills that are defective or of wrong construction, and containing any loose metal fittings or other devices likely to produce sparks under the influence of concussion or friction, must be set out of work, and not used again until put into perfect condition. All open lights (fireplaces, lamps, &c.) in the vicinity of the mills must be prohibited. No lights must be used inside the mills themselves except electric glow lamps, with double bulbs protected by wire gauze. All bronzes must be perfectly dry and properly warmed (with care) to the mill temperature before being fed to the mills; and any that have become dark coloured, and partly oxidised by moisture, must not be allowed to enter the mill, but be removed at once. All causes tending to humidify the air of the mill

rooms, or the walls and other objects, must be removed, and the mill rooms must be isolated from all others.

The danger arising in these mills could be minimised, and indeed obviated, were the air inside the mills replaced by some inert gas, poor in or devoid of oxygen, preferably by nitrogen (Rosenthal's German Patent, 75,797).

Above everything, all kind of electrical excitation in the mill must be prevented; for though the electric spark has little effect on bronze powder in a compact form, it may produce explosions when the powder is floating about as dust, especially when the latter is in rapid motion. When the dust is perfectly quiescent, nothing more than local ignition of a comparatively harmless character is produced, but as this is not transmitted through the entire mass of the dust, no explosion results.

The part played by the presence of an admixture of fat in bronze powder (see above) in the mills, has not yet been fully elucidated. It is not yet certain whether this fat diminishes the risk of explosion or (as might seem more probable) increases it. No regulations have so far been laid down on this point.

Equally undecided is the problem whether the risk is greater in the case of bronzes composed of one, two, or three metals.

The other stages of the manufacture of bronze powders present but little risk. Mention need only be made of the heating of the leaf metal to redness, and the rolling of the leaf metal, an operation attended with considerable heat and requiring an efficient cooling with water; further, the heating of the bronze, impregnated with  $\frac{1}{2}$  per cent. of paraffin, wax, or oil, in the production of annealing colours (*q.v.*).

Comparatively little risk attaches to the use of bronze powders, since, for the most part, the quantities used are small, and the dusting method, which might give rise to danger, is resorted to as little as possible, on account of the loss of material it involves. For the same reason "liquid bronzes" have been introduced, and are used in the form of "bronze tincture." One of these is "lustrogene," which consists of collodion or varnish containing aluminium powder in suspension.

The liquid vehicle used must be miscible with the invariably somewhat greasy bronze; and it must also dry quickly and be able to cement the bronze firmly on to the article coated. The fulfilment of the first two conditions constitutes a source of risk, inasmuch as liquids that mix with fatty matter and then dry quickly exhibit ready inflammability and volatility, conjoined with the formation of explosive vapours.

The liquids used in preparing bronze tincture (an erroneous title, seeing that the bronze is merely suspended and not dissolved), are frequently solutions of pyroxylin (an explosive nitrocellulose) in ether, of resin in benzol, or of celluloid in amyl acetate (Zapon lacquer).

Owing to the difficulty of mixing the bronze with the vehicle, trituration is necessary. This operation may generate frictional electricity (especially with solutions of resin in benzol), where the ether or benzine vapour is ignited; hence risk of explosion.

In many liquid bronzes the bronze separates out in course of time, and the tincture must then be shaken up for use. This has its objections, inasmuch as the gases form an explosive atmosphere within the vessel, and the operation of shaking generates electricity by the mutual

friction of the particles of bronze, the result being possibly an ignition and explosion of the mixture.

Even when no electrical excitation is produced, the employment of liquid bronzes in the presence of an open light or flame is always attended with considerable risk. The storage of liquid bronzes in shops, &c., should be subject to the same regulations as for preparations of benzol, ether, or like substances.

## 5. Metallic Sulphides

The compounds of metals with sulphur (which must not be confounded with those of the metals with sulphuric acid), present certain risks, owing to their active tendency to combine with oxygen. On exposure to the air in a freshly prepared condition, they absorb oxygen with avidity, as also when in a state of very fine division or mixed with fine carbon (lampblack); and should two of these conditions prevail simultaneously, the danger is increased.

In some cases the combination with oxygen proceeds so violently that spontaneous ignition ensues. The operation may, however, proceed quite slowly, *e.g.* in large heaps to which air gains access with difficulty, the interior of the heap often being entirely consumed without the faintest indication appearing on the outside (see *Coal*).

The most dangerous of the metallic sulphides are potassium sulphide (which has been called "pyrophor") sodium sulphide, barium sulphide, calcium sulphide, iron sulphide (*q.v.*), and copper sulphide.

The presence of carbon or moisture increases the danger of spontaneous ignition; and similarly carbon, lampblack, and charred organic substances are rendered liable to take fire spontaneously by the presence of a small quantity of metallic sulphide.

In contact with acids, these sulphides liberate inflammable sulphuretted hydrogen, which must therefore be carefully removed and rendered innocuous.

Metallic sulphides must be protected from damp, acids, and finely divided carbon; when freshly prepared they must be thoroughly cooled down before exposure to the air.

Potassium sulphide takes fire of itself in the air, and a similar behaviour is exhibited by sodium sulphide. Calcium sulphide (mostly a waste product) is the cause of outbreaks of fire in the waste heaps from alkali works, containing a good deal of carbon. These heaps should be well covered, to prevent the air penetrating to the interior.

Barium sulphide behaves in an analogous manner.

Iron sulphide (see under *Iron*) occurs in various forms of so-called pyrites (Marcasite, &c.). In presence of organic matter and moisture it is a frequent cause of spontaneous ignition (see *Coal*); and, though harmless in the compact state, it is liable to heat strongly when powdered, and then set fire to any organic matter present.

Dry iron sulphide ignites at 392° F., or at 320°–345° F. if in admixture with carbon. In many places "explosive pyrites" is encountered, which explodes when merely gently warmed. The only risk attaching to copper sulphide is that it becomes very hot, spontaneously, when stored in high heaps.

## CHAPTER LV

### ACIDS, OXIDES, SALTS

#### 1. Oxides

ALTHOUGH the following classification is no longer considered strictly correct, it is given here as sufficiently fulfilling the purpose now in view.

All the elements at present known on our planet may be divided into two principal groups:—

1. Non-metallic elements (non-metals and metalloids):

- (a) Hydrogen, oxygen.
- (b) Chlorine, bromine, iodine, fluorine (halogens).
- (c) Sulphur, selenium, tellurium (sulphur group).
- (d) Nitrogen, phosphorus, arsenic, antimony (nitrogen group).
- (e) Boron.
- (f) Carbon, silicon.

When the elements of groups (b), (c), (d), (e), (f), combine with oxygen, or those of group b with hydrogen, the resulting compounds are termed *acids*.

2. Metallic elements, (a) Potassium, sodium, lithium, rubidium, caesium (and ammonium) (so-called alkali metals).

- (b) Calcium, barium, strontium (metals of the alkaline earths).
- (c) Magnesium, beryllium, zinc, cadmium (magnesium group).
- (d) Aluminium, indium, gallium (aluminium group).
- (e) Cerium, lanthanum, didymium, yttrium, erbium (cerium group).
- (f) Iron.
- (g) Bismuth, vanadium, tantalum, niobium (vanadium group).
- (h) Tin, titanium, zirconium, thorium (tin group).
- (i) Lead, thallium (lead group).
- (k) Copper, nickel, cobalt, manganese (copper group).
- (l) Chromium, tungsten, molybdenum, uranium, mercury, silver (chromium group).
- (m) Gold, platinum, palladium, iridium, osmium, ruthenium, rhodium (gold group).

The elements of the groups 2 (a)–(d) are termed “light metals,” the others “heavy metals.”

When these metallic elements combine with oxygen, there results a base or oxide, which, according to the amount of oxygen absorbed, is termed:—

- Protoxide, or sub-oxide, containing the smallest amount of oxygen;
- Protoperoxide, with rather more;
- Oxide, or sesquioxide, with still more; and
- Peroxide (hyperoxide), containing the largest amount of oxygen.

Frequently these oxides are named “monoxide, dioxide, trioxide,” &c., according to the number of oxygen atoms present.

To the foregoing rules there are numerous exceptions. Thus, certain compounds of nitrogen are oxides, not acids; and certain compounds of

metals with oxygen form not merely oxides but also acids, per-acids, like chromic acid, permanganic acid.

## 2. Salts, Acids

The combination of an acid with an oxide forms a salt. According to the acid in question (the oxygen being a less decisive factor), salts exhibit special properties, of which the following may be mentioned, more particularly with reference to fire risk:—

(a) *Salts of Nitric Acid* (nitrates).

Chief representatives: saltpetre (potassium nitrate) and Chili salt-petre (sodium nitrate). They are rapidly decomposed by heating at 660°–930° F., and liberate oxygen at higher temperatures. They impart great inflammability to organic substances, and detonate in contact with glowing carbon (see *Chili Bags, Fireworks, Coloured Lights*).

(b) *Salts of Nitrous Acid* (nitrites).

Chief representative; sodium nitrite.

When heated, they liberate nitric oxide gas, which supports combustion like oxygen; any glowing substance immersed in this gas immediately bursts into flame.

(c) *Salts of Hyponitrous Acid* (hyponitrites).

Chief representatives: potassium and silver hyponitrites. They will not stand any great heat, the silver salt detonating at 302° F. Hyponitrous acid itself explodes under friction.

(d) *Salts of Sulphuric Acid* (sulphates).

These salts are not directly dangerous, but when calcined with charcoal they furnish the corresponding metallic sulphides (*q.v.*), some of which ignite spontaneously.

(e) *Salts of Chloric Acid* (chlorates).

Chief representative: potassium chlorate (*q.v.*).

All these salts are highly explosive and dangerous; the acid itself ignites organic matter at once.

Treated with sulphuric acid they furnish the explosive chlorine tetroxide. When warmed with carbon, sulphur, organic matter (especially of a combustible nature), compounds of cyanogen or sulphocyanogen, or manganese dioxide, they explode with violence. Similar explosions can be produced by friction, shock, percussion, or by breaking hardened fragments.

(f) *Salts of Perchloric Acid* (perchlorates).

These behave like chlorates, but are slightly less dangerous. Perchloric acid itself is spontaneously explosive when stored, or placed in contact with flame, carbon, ether, or any dangerous liquid.

(g) *Salts of Bromic Acid* (bromates), and

(h) *Salts of Iodic Acid* (iodates),

behave like chlorates, only with less violence.

(i) *Salts of Picric Acid* (picrates).

Chief representatives: potassium picrate and lead picrate. For these very explosive compounds, see *Picric Acid*.

(k) *Salts of Chromic Acid* (chromates).

Of themselves, these salts are harmless, but, when treated with sulphuric acid, they ignite any organic matter present.

Chromic acid also sets fire to organic matter, and explodes when suffused with alcohol or acetic acid.

(l) *Salts of Fulminic Acid* (fulminates).

These highly dangerous salts will explode on the slightest provocation.

Among other generally dangerous and explosive salts, mention may be made of the following :

(m) *Picraminates* : explode when warmed.

(n) *Sulphocyanides* (thiocyanates), explode when warmed with chlorates.

(o) *Styphnates* (oxypicrinates), like styphnic acid, explode on warming.

(p) *Permanganates*, when suffused with sulphuric acid, at once ignite any combustible substances present: ether, alcohol, inflammable gases, resins, oils, &c. Dry potassium permanganate suffused with glycerin, has a tendency to ignite spontaneously.

Permanganic acid itself explodes at 149° F., and ignites immediately on contact with paper, wood, oil, organic matter, or readily inflammable gases.

(q) *Propargylates* (propiolates), are explosive when warmed, the silver and copper salts in particular.

(r) *Oxalates* are harmless, except silver oxalate, which explodes when warmed.

From the foregoing particulars it will be easy to form some idea of the dangers that are incurred in the preparation and storage of salts (see also Table I.).

Several other acids and salts exhibit peculiar features in connection with fire risk, e.g. :

*Oxalic Acid*.—In the preparation of this acid from sawdust and caustic soda, large volumes of explosive oxyhydrogen gas are liberated at 392° F.; and though this reaction may be prevented by adding oils or vaseline, this addition results in the formation of inflammable hydrocarbon vapours, which may also prove dangerous.

The only dangerous oxalate is that of silver, which explodes on being rapidly warmed.

*Acetic Acid* (glacial acetic acid). B.p. 244½° F. Sp. gr. 1.055.

This acid forms an important constituent of wood vinegar (pyro-acetic acid), which also contains about 5–9 per cent. of wood spirit, acetone, and empyreumatic oils. Hence wood spirit is a dangerous liquid when distilled over lime, for the recovery of the bye-products, these latter furnishing explosive vapours.

The residual calcium acetate is purified by roasting at 390°–660° F., during which operation explosive vapours are liberated. If the heating be inadvertently carried too far, explosive vapours of acetone will be formed. Nitric acid is also dangerous to acetates, and where these or other salts are to be prepared, the added materials must never contain nitric acid, since the powerful oxidising action of same may produce extremely violent explosions.

The manufacture of acetic acid from wood spirit must be performed under observance of all precautionary regulations, and especially those relating to the prohibition of open lights and flame. Apart from the combustibility of its vapours, acetic acid is not dangerous, but its numerous bye-products are.

On the other hand, the recovery of acetic acid or vinegar, by the oxidation of alcoholic liquids, is perfectly safe, and is a process of fermentation. Though an accession of temperature is recorded during

the oxidation of the very dilute alcohol employed, it seldom exceeds  $104^{\circ}$  F.

The purest form of acetic acid is termed glacial acetic acid. The acid is fairly volatile, and the hot vapours are somewhat inflammable, but do not explode, whether alone or in admixture with air.

Whenever acetic acid or acetates are heated to  $660^{\circ}$  F. and over, the appearance of dangerous acetone is to be feared. Both acetic acid and its salts explode readily when mixed with chromic acid.

An important compound of acetic acid is amyl acetate, a readily combustible liquid, boiling at  $276\frac{3}{4}^{\circ}$  F., and furnishing inflammable vapours that form explosive mixtures with air. Care must be taken in the preparation to see that the amyl alcohol used does not take fire, and that the amyl acetate vapours are efficiently cooled.

Amyl acetate is often mixed with still more volatile liquids like alcohol, toluol, amylene (boiling at  $70^{\circ}$ – $97^{\circ}$  F.), its dangers being thereby augmented. To guard against risk, a guarantee of purity should always be demanded when purchasing amyl acetate.

In point of danger, amyl acetate is intermediate between alcohol and ether. It is largely used, instead of the last-named, for dissolving collodion wool, in the preparation of Zapon lacquer, in photography, in photometry (gas testing), and is said to be employed in the manufacture of liqueurs.

*Sodium Nitrite.*—This salt gives off oxygen when heated; and its preparation is not without danger, being effected by heating Chili saltpetre to  $750^{\circ}$ – $930^{\circ}$  F. in presence of lead. Explosive detonations readily occur at these high temperatures; and the bottom of the pan is liable to burn through in consequence of overheating. Sodium nitrite must not be fused along with ammonia salts, or mixed with cyanogen compounds, since in both cases violent explosions ensue.

*Cyanogen Compounds.*—Carbon and nitrogen combine to form cyanogen, a combustible gas which forms with chlorine a liquid (cyanogen chloride) that boils at  $60^{\circ}$  F.

With hydrogen, cyanogen combines to form hydrocyanic acid (prussic acid, formonitrile), a readily combustible liquid, boiling at  $79\frac{3}{4}^{\circ}$  F., the volatile vapours of which have the density 0.700.

The preparation of this acid is often attended with risk; cyanogen and hydrogen gas being heated to  $930^{\circ}$  F., or combined by the passage of electric sparks. Another method is to explode acetylene and nitrogen, or pass electric sparks through the mixture. A readily inflammable and combustible mixture of gases is left.

The compounds of cyanogen with metals (cyanides), of which potassium cyanide is an example, are prepared, at red heat ( $930^{\circ}$ – $1650^{\circ}$  F.) from charcoal, potash, soda, nitrogenous substances (like leather, offal, sugar-beet waste), often with addition of carbides. These processes are dangerous, the calcination of the organic matter furnishing inflammable gases and vapours and gases, which are passed through a system of flues heated to about  $2000^{\circ}$  F.

When cyanides are heated to  $930^{\circ}$  F. in air, in presence of manganese dioxide or minium (*i.e.* carriers of oxygen), they undergo conversion into cyanates.

Potassium cyanide and sulphur fused together furnish *potassium sulphocyanide* (thiocyanate), which, though harmless in itself, furnishes

when fused or even intimately mixed with saltpetre or chlorates, a highly explosive substance, which can be exploded by flame, incandescent bodies, sparks, or a temperature of  $750^{\circ}$  F., but not by shock or percussion.

In combination with iron and potassium, cyanogen forms the important substances :

*Potassium ferrocyanide*, or yellow prussiate of potash, and

*Potassium ferricyanide*, or red prussiate.

The latter is prepared in a perfectly safe manner from the yellow salt. On the other hand, the manufacture of the yellow prussiate by fusing iron and potash at dull red heat with leather, rags, horn, hoofs, sinews, flesh, blood, wool, &c., is not free from danger, owing to the resulting formation of inflammable and explosive vapours.

The process is carried out on a large scale. The charging of the furnace with fresh material is attended with danger of flaming explosion of the gases, which contain a large proportion of carbon monoxide.

The melt prepared in the furnace is rich in carbon monoxide, and, should the furnace be opened prematurely, the admission of air may lead to spontaneous ignition of the carbon, or semi-carbonised raw materials, to the great prejudice of the manufacturer.

Several other processes are practised, but all of them are attended with calcination at high temperatures, the formation of vapours containing carbon monoxide, and are of a more or less explosive character. Prussiate is also obtained from the spent purifying materials from gas-works ; but, though in this case calcination is unnecessary, dangerous solvents, like carbon disulphide (*q.v.*), have to be employed.

*Alum* (Potassium-aluminium sulphate, *Alumina Kali sulfuricum*), fusing point  $197\frac{1}{2}^{\circ}$  F.

This salt, though otherwise perfectly safe, and even becoming fire-proof when heated to incandescence, exhibits two peculiarities, on account of which it must be mentioned here.

It is a frequent practice to fill the interior of hollow, cast-iron cylinders, shafting, and other revolving hollow bodies, with alum, in order to prevent distortion of the metal. In this casting process, which entails protracted heating at  $172\frac{1}{2}^{\circ}$  F., the alum separates into two compounds, containing different proportions of water. The one richer in water solidifies on cooling, but if then exposed to vibration, shock, &c., sustains considerable alterations, greatly increasing in volume and becoming an opaque mass. These alterations, and especially the expansion, occur so rapidly and generate so much heat, that the surrounding hollow body is sometimes burst with violence. A large hollow shaft filled with alum has been known to explode from this cause ; such explosions, however, do not produce outbreaks of fire.

When alum is calcined with charcoal, the mass ignites spontaneously in air, owing to the presence of potassium sulphide.

In the preparation of alum from alum shale, the raw material must be well looked after, on account of its content of pyrites and bitumen, and must be sheltered from the wet, since, like coal, it is liable to spontaneous ignition.

# PART XI—DANGERS CAUSED BY LIGHTNING, FLASHING AND LIGHTING MATERIALS, AND BENGAL LIGHTS

## CHAPTER LVI

### DANGERS FROM LIGHTNING

THE increased violence of lightning accidents (not their frequency) observed during recent years, is more attributable to altered conditions of water and drainage, the more extensive erection of iron structures, complicated architectural decorations, deforestation, and bad lightning conductors, *i.e.* to telluric factors, rather than to meteorological (atmospherical) conditions.

Considerable differences of opinion still prevail as to the best methods of guarding against lightning, as is only natural in view of the incomprehensible behaviour of the lightning itself. Thus instances have been known where lightning has penetrated the strongest casement walls, and yet left unconsumed powder lying in a loose condition close by; or has melted bells and left the wooden belfry intact.

In view of such paradoxical behaviour of lightning, it is impossible to lay down hard and fast rules suitable for all conditions; and we shall therefore merely sketch the broad measures now regarded as generally applicable, leaving the details to be modified according to local circumstances.

1. It is better for any building, factories in particular, to be without any lightning conductors at all than to be fitted with such as are defective or badly planned.

The purpose of a lightning conductor is not so much to attract a lightning flash and conduct it to earth, as to facilitate the equilibration of terrestrial and atmospheric electricity in good time, long before the two electricities attain a dangerous tension. In fact, a lightning conductor discharges functions similar to those of a safety valve, which enables the steam to escape from the boiler before it has attained an explosive pressure therein.

If, in consequence of defective installation, a lightning conductor is unable to effect this mutual equilibration of atmospheric and terrestrial electricity, it is far less able to perform the further task of conducting high tension electricity in a manner ensuring protection to life and property; and is, in fact, rather a source of danger than otherwise.

2. A lightning conductor must be installed in such a manner as to

protect the entire building, in all its parts, and also the immediate vicinity of the structure.

This protection will only be afforded when the chimneys, roofs, garrets, flag-posts, gutters, air vanes, ventilating and furnace pipes, metal doors, iron gratings, water and gas pipes, and electric wires—in fact, all projecting portions of the building, and all external and internal conductors—are included in the area protected by the lightning conductor in question.

By the *protected area* is understood the conical space equal in height to the distance between the ground and the point of the conductor, and with a base comprising a circle with a diameter twice the height of the lightning rod. The apex of this cone coincides with the point of the rod, and, if the conductor be properly installed, everything within this area will be protected. The height of the rod is determined by the length of the roof; if the latter be 45 feet long, a 15-foot rod will suffice, but it must be erected mid-way along the roof. In the case of very long, straight roofs, a number of rods must be provided at intervals not exceeding four times their vertical height; and the rods at each end of the row must not be more than one-and-a-half times their own height away from the ends of the roof.

The protected area may be enlarged by increasing the height of the rods, or providing a larger number. The latter arrangement is preferable for buildings containing large masses of metal, numerous decorations or projections, and complex exteriors or broad roof areas. With a large number of rods a more regular discharge can be ensured, partial discharges being effected, of a far safer and less dangerous character than a total discharge by a single rod. Even if the latter be made ever so long, it will always allow the tension to become higher than when several rods are used. Of course, all the rods must be in good conductive connection with each other.

All roof projections in the vicinity of lightning rods must be put in communication with the latter, since otherwise the lightning may spring from the rod on to the projections in question; and this tendency to diverge from the prescribed path forms one of the greatest dangers of defective lightning rods. (See *Short Circuiting*.)

Where the lightning rod of any building allows such short circuiting to occur, it must be replaced by a better one, the danger becoming more imminent with every recurring storm.

The method of bringing the said projections into conductive connection with the lightning rods will depend on local conditions.

3. The erection of lightning rods must be entrusted to a properly skilled person only, and one capable of applying the laws of science in a rational manner and in accordance with the local circumstances.

4. The following points must be borne in mind in the erection of lightning conductors:—

(a) The points of the rods must be made of rustless and highly infusible metal, able to withstand moisture, smoke (sulphur dioxide), products of combustion, gases, and vapours, namely: gold, silver, platinum, nickel, and well gilded or nickelled copper. For factory chimneys, prepared retort graphite is also suitable.

When nickel is used, it must be chemically pure and of sufficient thickness.

(b) The rods must be of metal, thick enough to prevent fusion by the lightning; they must project at least 40 inches above any object in the immediate vicinity.

(c) The conductor, *i.e.* the bridge for conveying the lightning to earth, must be of sufficient dimensions to convey a larger amount of electricity than is contained in a flash of lightning. It must be made of a good conducting metal, preferably copper. Iron of sufficient thickness is also permissible, but not brass, lead, tin, or zinc. Copper conductors must be at least one-third of an inch thick, those of iron not less than three-fifths of an inch; in any event the conductor should not be fused or even heated to redness by the flash.

The form of the conductor, whether ribbon, one or more ply wire, straight, or twisted, is less material than sufficient thickness.

(d) The continuity of the metal forming the conductor must not be interrupted; hence broken conductors must be repaired by careful brazing and not by merely lapping, twisting, or tying the broken ends.

(e) In passing round corners, &c., the conductor must be given merely a gentle bend or arch, and never turned at sharp angles; and the direction must always be continuously downward, free from any upward bends.

(f) The conductor must be thoroughly insulated from the point to the grounding plate, and must be kept out of all contact with any conducting materials. Special attention must be devoted to the insulation (by porcelain or glass rings) at all guides and supports in bends.

(g) The conductor should be erected on that side of the building which is most exposed to the weather and rain, since the wetter the conductor the better it will discharge its functions.

(h) Wherever possible it is preferable to attach the lower end in metallic connection with the town water mains, not merely by winding it several turns round the pipe, but also by soldering; and that too with solder capable of permanent sojourn in damp earth (ordinary tinman's solder is unsuitable). The contact surfaces of the conductor and water main must be made bright before being soldered.

It is advisable to have these soldered connections in an accessible position, so that they can be inspected, in the event of a violent flash, to ascertain whether any damage has been done to the soldered connection or the joints of the main. It is not advisable to connect lightning conductors to gas mains, for in the event of a defective spot in the main—and gas pipes are not invariably free from leaks—the gas may be ignited, and at the same time the lightning may be conducted to a neighbouring gas meter or gas engine, and considerable damage be occasioned. Notwithstanding this, the use of gas mains for this purpose has been frequently advocated.

(i) If no water or gas main be available, the lower end of the conductor must be connected to a metal plate, about 6 sq. ft. in area, and grounded about 6 ft. deep in the soil or in the soil water. The popular practice of grounding the conductor in a well, especially when this is sunk in the cellar, is very dangerous.

The metal grounding plate and conductor must be brightly polished at the surfaces united by soldering. The plate must not be rolled, but must extend vertically downwards into the soil water, and be at least 10 ft. away from the foundation of the building, and must never be placed where the ground is quite dry.

If the ground water cannot be encountered, the conductor must be divided into four at the lower extremity of the lightning rod (the collector), each portion of the conductor being then carried symmetrically down the four sides of the building and grounded by means of metal plates, the latter being then placed in mutual connection by an underground wire.

Although this method increases the expense and complexity of the installation, it is the only one ensuring safety where the soil water cannot be tapped, the establishment of connection between the lightning rod and the soil water—or the replacing of such connection by the method indicated—being a fundamental principle for obtaining protection from lightning.

(k) Grounding plates must never be sunk close to the place where the branch water pipe for supplying the building issues from the main, otherwise the lightning may pass along this branch pipe into the building.

(l) Experience has shown that isolated buildings that are fitted with lightning conductors, and have remained undamaged for many years, have suffered injury shortly after water or gas has been laid on, the lightning having jumped (lateral discharge) from the conductor to the branch water or gas pipes. Instances of this kind are afforded by churches at Greifswald and Stralsund, school buildings at Itzehoe, Count von Seefeld's castle, houses in Basle, Graz, and elsewhere, gas explosions having been produced. These lateral discharges indicate that the lightning has found a better conductor in the gas or water pipes than is afforded by the lightning rod. Hence installations of this latter kind can only be effectual when *they* themselves constitute the best means of conveying the electric current in question. To obviate the danger of these lateral discharges—which are sometimes the cause of far more damage than direct lightning strokes—the highest points of the gas and water pipes should be connected with the lightning conductor in a suitable manner.

5. The lightning conductor must be kept in good condition and tested on a fine spring day. Summer tests are unreliable and lead to erroneous results, on account of the great electrical excitation of the atmosphere at that time of year.

The usual galvanometer test merely indicates whether the aerial portion of the installation is in good working order. This, however, is insufficient; the test must also show whether the earth contact is still good and the entire installation capable of safely drawing off powerful flashes without risk of lateral discharge.

These tests must be performed with a rheostat and a provisional grounding plate, embedded in the earth a short distance away from the building. Such tests are highly essential in the case of premises needing special protection from lightning on account of the materials worked or stored; and insurance companies should never rest satisfied with the simple galvanometer tests.

6. In addition to the annual test in spring, other tests should be performed after a stroke of lightning has occurred or when a new conductor has been installed. In this case, the condition of the collecting rods must be specially examined, since these generally suffer severely when struck.

7. In judging the danger from lightning, the following local conditions should be taken into consideration:—

The danger is heightened by:

A high and isolated situation of the building.

High projecting portions of the roof, flag-posts, and weather vanes.

Very steep or slightly pitched roofs, high gables in particular.

Smoky chimneys.

Well shafts, and shafts in or near the building.

Lift shafts, chains hanging in doorways or from cranes.

Bells and bell-ropes, bell-ringing (this should be prohibited during thunder-storms).

Old, useless lightning conductors.

The vicinity of rivers, stagnant water, and isolated trees.

Trees with dead branches.

The trees most liable to be struck by lightning while green, are: oak, poplar, and other foliaceous trees; then conifers, and, lastly, beech. Among the coniferæ, the order runs: Scotch fir, most; then ordinary fir, and, lastly, pitch pine.

Taking the danger run by beech trees as unity, the proportion for coniferæ is 14; for deciduous trees generally, 39; and for oak, 46.

The more wide spreading the branches, the greater the risk incurred by the tree; and the same applies to the proportion of dead branches in any tree. Hence, the dead branches should always be removed from trees in the vicinity of dwellings, to prevent the possibility of lightning jumping from such dead branches to the house. Various explanations have been offered for the different susceptibility of the several kinds of trees to lightning. Thus, it is stated that the leaf hairs—especially in the very hairy leaves of the foliage of the beech—present a timely means of escape for the electricity, before it has time to attain a dangerous tension; whilst others lay stress on the conductive capacity of the wood and the presence of fat or oil therein.

These explanations have been more or less confirmed by facts gleaned from practical experience. The fat theory seems most probable, the danger from lightning diminishing as the proportion of fat increases. On the basis of several thousand observations, the lightning risk of trees has been classified as follows:—

Smallest in the deciduous trees	$\left. \begin{array}{l} \text{beech} \\ \text{lime} \\ \text{walnut} \\ \text{birch} \end{array} \right\}$	trees very rich in fat.
Medium in the coniferæ	$\left. \begin{array}{l} \text{pitch pine} \\ \text{fir} \\ \text{Scotch fir} \end{array} \right\}$	trees with a medium fat content.
Greatest in the deciduous trees	$\left. \begin{array}{l} \text{ash} \\ \text{elm} \\ \text{maple} \\ \text{oak} \end{array} \right\}$	trees poor in fat.

The class of soil also has an influence on the risk from lightning, which strikes most frequently in loam, less often in sand; still less in clay; then in Keuper marl; and least of all in calcareous soil. The ratio

in this case is approximately as follows, the smallest risk being placed first:—

Calcareous soil, 1	Clay soil, . . 7	Loamy soil, . . 22
Keuper marl, . 2	Sandy soil, . . 9	

Asphalt flooring or pavement is almost perfectly lightning-proof, asphalt being a non-conductor. A whole house may be rendered fairly proof against lightning by completely insulating it, cellar and all, floor and walls, by a thick layer of asphalt.

Large towns form almost lightning-proof oases, the environs being less secure, the storm mostly spending itself there. On the other hand, small villages are still less safe, and flat land is more endangered than any other. Hills and mountainous districts are safer from lightning than plains; but if traversed by a broad river, the latter forms a pathway preferentially chosen by storms, in which event the land on either bank is more endangered than flat territory.

Dangerous premises (nitrating works, powder factories, blasting-explosives factories and firework manufactories) should not be fitted direct with lightning conductors, but the latter should be situated on the surrounding walls or mounds, and carried to a sufficient height to afford protection to the entire premises. Special protection should be afforded to the buildings by laying the foundations on an insulating stratum of good natural asphalt. As a further precaution, the whole of the different lightning conductors may be connected together by a wire network of sufficient dimensions.

Railway trains are almost lightning-proof, and even should a flash strike, it would find such a ready escape through the rails, &c., that damage would seldom occur; fires, never.

On the other hand, lightning is a source of danger to telegraph wires, and still more so to those of the telephone and to the premises connected by the latter. In the former case, the danger is almost entirely obviated by the provision of efficient lightning conductors, which rarely allow a flash to gain access to the buildings. The use of telephones should be prohibited during thunderstorms.

Animals are all equally liable to be struck by lightning; at least no difference in predisposition or immunity in the various races has yet been detected.

Insured animals that have been struck by lightning may be used for food if, on being stuck immediately afterwards, a copious flow of blood is observed. Should, on the other hand, the escape of blood be scanty, the carcase must only be used for manure, &c.

## CHAPTER LVII

## FLASHLIGHTS

THIS name is applied to preparations that are consumed with a flashing emission of light when ignited. Such preparations are now widely produced on a large scale, and employed for many purposes: photography, hunting, illumination, signalling, fireworks, and stage effects.

The lighting materials consist of flash powder, flash paper, flash matches, or flash pellets, all exhibiting more or less dangerous properties. As single articles they are mostly harmless, but are on a par with blasting explosives when present in large quantities.

The production of a flashlight is based on the combustion of an easy and rapid-burning substance in the presence of a carrier of oxygen (*q.v.*). The heating power of the flashing material must be very great, in order that it may induce the carrier of oxygen to rapidly and, indeed, instantaneously liberate that gas, the presence of an atmosphere of oxygen being essential to the intensity of the resulting light.

Premier place among the flashlight preparations is maintained by metallic magnesium in the form of an extremely fine powder. This metal ignites readily at any flame, and burns with a puff and an abundant emission of light. To intensify the effect, the metal is mixed with carriers of oxygen, like potassium permanganate, manganese dioxide, barium peroxide, potassium chlorate, gunpowder, antimony sulphide, guncotton, colophony, lycopodium, shellac, dextrin (magnesium fans), and occasionally phosphorus.

These mixtures are generally stable, the keeping properties having been tested up to seven years. This is an important factor, since spontaneous ignition might lead to very serious consequences. Nevertheless, insurance companies should be expressly warned against attaching any value to these observations when the materials are not chemically pure. Inferior and technically impure ingredients are prone to spontaneous ignition and its dangers. Old mixtures should not be accepted as insurance risks; or a time limit should be fixed beyond which these mixtures would cease to be insurable.

The mixtures may be ignited (and exploded) either by flame, sparks, red heat, sudden heating, shock, fall, or friction.

Owing to the difficult combustibility of the liberated gases and vapours, such explosions do not cause much damage; when the mass is not considerable, even panes of glass will stand the effects of the explosion. On the other hand, the high temperature of the explosive reaction greatly increases the tendency of these otherwise gentle explosions to lead to an outbreak of fire (Bayreuth Carnival, 1893).

When such explosions do occur, the employment of extinguishing agents and the performance of rescue work become impracticable, by reason of the extremely troublesome and irritating coughing and asphyxiation produced by the fumes, which renders a sojourn in such an atmosphere impossible.

To accelerate the ignition, flashlight preparations are often suffused with benzol or ether—a very dangerous practice, and one likely to engender spontaneous ignition, or even explosion, when the preparation is already in a state of incipient decomposition. In fact, the use and handling of flashlight preparations in presence of such dangerous liquids is open to serious objection all round.

The preparations are ignited by direct contact with flame, or else by blowing the atomised mixture into a flame, *i.e.* a kind of dust explosion!

The pressure exerted in blowing must be considerable, since, if too weak, the lighting back of the flame might cause serious accident.

The manufacture of flashlight preparations on the large scale is a very dangerous process. The most scrupulous care and order must be everywhere observed; the waste products stowed away with special caution, and, of course, in a fireproof place; metallic tools, liable to strike sparks, must be banished completely, and all violent friction, shock, open lights, or fire avoided.

The amount of substance taken at a time should not exceed 5–7 lbs. On account of the risk of spontaneous ignition with advancing age, each large package of finished flashlight material should be stamped with the date of manufacture, so that such as have got past the time limit may be excluded from insurance.

Aluminium powder is also used as a flashlight material in conjunction with carriers of oxygen. These mixtures are no less dangerous or more stable than those containing magnesium, and should, like them, not be mixed until just before use.

In point of ignitibility they are on a par with the magnesium preparations, and all that has already been said with regard to aluminium bronzes, especially in respect of moisture, applies here, perfectly dry storage, with complete exclusion of damp, being essential, or highly dangerous spontaneous ignition will be certain to occur.

Danger may also arise from the lamps in which these flashlight preparations are consumed. Numerous types of these lamps are known, but only the very best should be used, defective construction being a frequent source of explosions.

When the powdered form of flashlight preparations is not suitable, it is usual to impregnate some solid substance, generally in a superficial manner, or else the mixture is packed in cartridges. Impregnated matches and strips of paper are also manufactured for the same purpose.

All of these are fairly safe in small quantities, but exhibit in bulk the same dangers as the powders. Special care must be taken to prevent mutual friction.

Flashlight paper usually consists of nitrated paper (*q.v.*), prepared by immersion in concentrated nitric acid, followed by washing and careful drying. It explodes on percussion.

Flashlight matches are made of strips of wood or millboard, the charge being inserted in holes punched for this purpose, and kept in position by covering strips of gummed satin paper. The paper is coated externally with an igniting composition.

## CHAPTER LVIII

## FIRE LIGHTERS, FUZES, MATCHES

## 1. Fire Lighters and Fuzes

**FIRE Lighters** are generally made of woody or strawlike substances (sawdust, wood wool, shavings, and waste wood), peat, fir cones, paper, millboard, maize cobs, &c., superficially impregnated with liquid resin, tar, or paraffin.

The process is a somewhat dangerous one, owing to the necessity for melting the impregnating materials, which then give off inflammable vapours. The risk is increased by the generally primitive plant employed, the use of open fires rendering proper control of the temperature impossible.

To facilitate the compression of the materials, sawdust in particular (see *Wood*), they are usually damped, which readily leads to spontaneous ignition. Equally dangerous is the practice of storing the freshly made, resinous, oily products in large heaps, which are also liable to take fire spontaneously. Well-ventilated storage should be provided, and high storage pressure avoided.

**Fire-lighter Cakes** are made by dipping dried fir cones, or maize cobs, in hot tar.

**Igniting Pellets** for fireworks consist of very sensitive mixtures, mostly of antimony sulphide and potassium chlorate, or the latter and phosphorus. These pellets must not be knocked, triturated, or brought in contact with flame or sparks, nor should they be exposed to the sun, or they will explode.

**Fuzes** are made of cotton threads impregnated with fine gunpowder; or cords of guncotton or diazobenzolsulphonic acid. They possess very dangerous characteristics, and are particularly susceptible to the influence of fire.

Fuzes of diazobenzolsulphonic acid (see *Diazobenzol*) have the great advantage of burning without any flame or visible glow. On this account they may be safely used for blasting operations in places where explosive gases, vapours, or dust are produced.

**Paper Caps** (amorces) for toy pistols, detonating bon-bons, and detonating pillules, are masses containing fulminates and spread on paper or applied in any other way, so that they necessarily explode when subjected to friction, percussion, or when thrown down. The active ingredient is mercury fulminate, and therefore highly explosive.

Danger is only incurred when large quantities are in question. Explosions of the packages have been known to occur (*e.g.* at the Coburg railway station) when shaken in transit or dropped, although the contents had been packed with all care.

In preparations where the mass is applied in little dabs on sheets of paper, even the slightest friction is enough to produce an explosion. Thus, it is dangerous to draw one of these sheets out of a pile, on account

of the resulting friction with the overlying sheet. These explosions mostly produce an outbreak of fire, owing to the burning of the paper. Special danger attaches to the storage of such sheets in toy shops, which, being also stocked with varnished wooden toys and articles covered with hair, wool, and other fibrous materials, form bad insurance risks. In these stores, great care should be taken when large quantities of sheet caps and detonators are kept.

## 2. Matches

The match is the most frequently used, and misused, of all fire-lighters. Statistical reports show that, in certain years, 80 per cent. of the total outbreaks of fire were caused by matches, either dropped and trodden on, thrown down whilst still glowing, or used as play-things by children. The latter contingency frequently arises in farmsteads.

In view of their danger, the carrying and use of matches should be prohibited in all premises where dangerous materials are treated or stored, *e.g.* where explosive substances, liquids, dust, gases, or vapours are produced or inflammable raw materials worked. The same prohibition should also extend to workmen clad in garments that are soaked with oil and contaminated with organic dust.

The best means of preventing the carrying of matches is the provision of working clothes without pockets. Factory regulations should include clauses forbidding the carrying of matches, especially loose, and in all cases where smoking or the use of open fires or lights is prohibited.

The ignition temperature of matches fluctuates between 140° and 285° F., special risk attaching to matches that ignite below 212° F. A still more important factor, however, is the quantity of matches present. Though it is feasible to assume that, as the occurrence of danger depends on the ignition of a single match, the presence of one match is just as dangerous as a thousand, this is not quite accurate, experience having shown that a single match requires a far higher temperature for its ignition than a boxful.

By itself, a single match presents a large cooling surface, and hence is less subject to the effects of a given degree of warmth than when a thousand matches are packed together, these being more able to accumulate heat, and less exposed to surface cooling. The case is analogous to that of phosphorus. If a pound of phosphorus in one lump be exposed to the same amount of heat as another pound divided into 500 portions, the former will take fire quickly, while the 500 pieces will remain unaltered for some considerable time.

Thus the danger of a box of matches, as compared with that of a single match, does not depend on the number of matches it contains, but on the fact that this aggregation, requiring less heat, will ignite much earlier and thus produce damage where one match would be perfectly harmless. This condition obtains in all kinds of matches, but is more accentuated in phosphorus matches than in Swedish or safety matches.

At the present time there are three chief commercial varieties of the match; headless matches, Swedish (safety) matches, and phosphorus matches.

(a) The composition for **Headless Matches** mainly consists of the very dangerous barium chlorate (see *Chlorates*), or of the equally explosive barium bromate.

These matches present great advantages over other kinds, both from the maker's point of view and that of the consumer. They are extremely cheap to manufacture, there being no need for the impregnation with paraffin, the preparation of a complex igniting composition, or the dipping in sulphur and phosphorus. In addition, there is no afterglow once the flame is extinguished.

On the other hand, the composition, which is merely a solution of a single ingredient, is excessively sensitive to friction or shock, and is liable to produce explosions which may attain serious proportions when the number of matches concerned is large.

Another source of danger in these matches is the circumstance that there is nothing in their external appearance to betray their character as matches that require careful handling; they have no heads, and at first sight it is difficult to say which is the striking end.

In the case of all other kinds of matches, one can see at once what they are and whether they have been struck; hence they are usually handled and stored with care; but with these headless matches, which resemble an ordinary piece of wood, such precautions are not employed, there being nothing to show their dangerous nature. True, the igniting end is rounded off a little, but this is not a sufficient indication.

Consequently it is urgently necessary that the employment, storage, and private use of such matches should be strictly prohibited in all works; and, apart from their explosibility, their poisonous nature affords an additional reason for their banishment from commerce.

(b) **Swedish or Safety Matches.**—For these matches two compositions are required; an igniting medium and a frictional medium. The former chiefly consists of prepared carriers of oxygen, especially potassium chlorate or manganese dioxide, the explosive character of which has been greatly reduced by an admixture of inert adjuncts. The friction composition is mostly red phosphorus, with small additions.

At least, this was formerly the case, when Swedish matches really deserved the title of safety matches and would ignite on the specially prepared friction composition only; but nowadays, almost every *soi-disant* "safety match" will ignite when rubbed on nearly any surface, especially on smooth hard paper or wood, slightly roughened stone, if not too soft, or roughened glass, provided a rubbing surface of about 12–20 inches in length is available. Indeed some of these matches have been known to strike when rubbed on the paper label surrounding the box, thus rendering any "prepared surface" unnecessary.

It is assumed—and this is probably correct—that the property of such "safety matches" of striking on other surfaces is due to the white phosphorus they contain. The veritable "safety" of the Swedish match, *utan svävel og fosfor*, is a thing of the past, or nearly so, though these matches are still less dangerous than the phosphorus matches.

To strike these matches on any other than the prepared surface requires some practice, and an outlay of strength that is not possessed by children; and, besides, they are less liable to ignite by the influence of certain forms of heat, *e.g.* the sun's rays, than phosphorus matches.

They ignite only at 320° F., whilst phosphorus matches light at a temperature of 113°–140° F. When trodden under foot, they light less readily than phosphorus matches, and not at all on soft flooring. They are not carried loose in the pocket, but kept in the box, and they are less frequently lost or strewn about than phosphorus matches.

In general, therefore, preference should be accorded to the Swedish match, as less dangerous than its phosphorus competitor. This, however, applies only to matches as articles of storage, and before they are struck. On the other hand, if the two kinds of matches be struck, and then compared, it will be found that the Swedish match is by far the more dangerous, possessing the objectionable property of retaining prolonged incandescence in the charred head in such a manner that this condition cannot be clearly observed externally; whereas the head of the phosphorus match goes out immediately, and is already cold by the time the match has finished burning, the porous head of the Swedish match remains aglow for some time. True, one can take hold of the head between the fingers, but if it be crushed, a sharp sensation of burning will be felt.

Highly divergent results have been obtained by comparative tests with different kinds of Swedish matches, but in general the burnt heads remain dangerous for 2–3 minutes. In presence of a slight draught the author succeeded in charring and glimmering combustible fibres with the heads of extinguished Swedish matches within the specified period, and in several instances it was found possible to relight a tobacco pipe by pressing the glowing match head down into the bowl.

Great progress has been made in obviating these risks; but the improvement has not extended to all makes of Swedish matches, there being still a large number capable of doing great damage, owing to the unfortunate property aforesaid.

Another very dangerous property of these matches has now been eliminated, and that is the tendency of the head to drop while the match is still burning, or directly after, a behaviour that is now confined to the inferior makes. The danger of these glowing heads was the more acute in that attention was chiefly devoted to the ignition of the stick, leaving the insignificant head out of consideration. The author has tested about 150 different makes of Swedish matches, but only in a few isolated instances was any breaking off or falling of the head discernible, although provoked by intentional carelessness in striking.

With regard to the after-glowing of the sticks, which has been observed to continue for 2–3 minutes in windy weather, it may be stated that experience has shown that flat sticks go out more quickly than the stronger square ones, even in a high wind.<sup>1</sup> Safety matches are now made (by Garber's process) which, instead of being extinguished by a high wind, actually require a strong breeze to make them blaze up. The composition is prepared from potassium chlorate and red phosphorus, together with gum, starch, &c.; the resistance to combustion

<sup>1</sup> *Translator's Note.*—Numerous brands of safety matches now on the market are guaranteed not to glow after extinction, the wood being impregnated with a view to remove this undesirable feature.

being obtained by fine grinding, and the method of mixing the chief and supplementary ingredients. Such matches are naturally more dangerous than the ordinary kinds, which are easily extinguished by a light puff of wind.

Though the ingredients used in the manufacture of Swedish matches are of a dangerous character, the risks of the operation can be greatly diminished by the employment of carefully designed plant and proper control, special attention being devoted to the isolation of the materials, the various processes and the workrooms, in respect of which it is impossible to be too careful.

The materials are: potassium chlorate (principally), manganese dioxide, sulphur, minium (red lead), antimony sulphide, paraffin, and the inert substances: glue, gum, and glass powder.

To protect the match heads they are sometimes dipped, while still moist, into aluminium powder (bronze) to form a covering. This practice is not altogether free from objection, because of the danger caused, firstly, by moistening the bronze powder; and, secondly, by bringing the same into such intimate contact with carriers of oxygen (potassium chlorate).

The chief danger is in mixing the potassium chlorate with the carriers of oxygen and the sulphur, owing to the tendency to explode when triturated. The mixing must be performed in a damp state.

In a few factories it is still customary to use the highly dangerous nitromannite and potassium picrate, the natural result being a greatly increased risk, especially as regards explosion.

The preparation of the composition for the rubbing surface is attended with risk, on account of the conversion of white phosphorus into the red variety by heating it to 445°–480° F. in closed vessels. Generally, however, the red phosphorus is bought ready made, and in such cases the risk is small, unless there be any white phosphorus (*q.v.*) still present, as may often happen if the white phosphorus has been too strongly heated. Antimony sulphide also is used in the preparation of the friction surface, without any increase in the risk. Of late, however, potassium chlorate, saltpetre, potassium chromate, and lead peroxide are added to the composition, and augment the dangers of the process; but the quantities used are only small.

(c) The **phosphorus match** industry has suffered a decline of prosperity, owing to the unhealthy character of the work and the competition of the Swedish matches.

The principal ingredient is phosphorus, the manufacture of which is in the hands of a few special factories. The process is a very dangerous one, owing to the high temperatures (975°–1830° F.) used in treating the raw material, bones (calcium phosphate), with charcoal, and also owing to the exceeding inflammability of the phosphorus. At present phosphorus is manufactured in the electric furnace, also at high temperatures, calcium carbide (*q.v.*) being formed as a dangerous waste product. This electrical method seems to have a great future before it, and likely to extend the phosphorus industry.

Phosphorus is readily ignited at 140° F.; in large (1 lb.) lumps it even ignites spontaneously when exposed to direct sunlight; and for this reason is generally cast in thin sticks. When dissolved, *e.g.* in carbon disulphide, and a few drops are allowed to evaporate, the residual

thin stratum of phosphorus is equally liable to take fire spontaneously, especially in the sunlight. Phosphorus explodes when warmed along with sulphur, and will explode on admixture with carriers of oxygen, peroxides (lead peroxide), or ozone. Any strong friction will set fire to phosphorus.

If several small pieces of phosphorus, that on exposure singly to the air would scarcely sustain any alteration, be united into a single heap, they will then, in that state, ignite spontaneously, just like a single lump of equal size, and quickly take fire on exposure to the sun.

The spontaneous ignition of phosphorus is purely a phenomenon of oxidation, combination with oxygen accompanied by the generation of heat, which, in the case of large pieces of phosphorus, is prevented from escaping by the insufficient surface for radiation. Small lumps accumulate less heat, being more effectually cooled by the air.

Phosphorus melts at  $111\frac{1}{4}^{\circ}$  F., ignites at  $140^{\circ}$ – $143\frac{1}{2}^{\circ}$  F. (according to the researches of F. Eydmann, as low as  $113^{\circ}$  F.), and boils at  $554^{\circ}$  F. (of course, out of contact with air, otherwise it would burn). It must be melted under water. When heated to  $445^{\circ}$ – $480^{\circ}$  F. in closed vessels, the ordinary or "white" phosphorus passes over into the "red" modification, reverting to its original condition if heated still further to  $500^{\circ}$ – $550^{\circ}$  F.

When pure, red or "amorphous" phosphorus is not inflammable, and does not take fire until heated to  $464^{\circ}$  F. in the air. It can, however, only be regarded as perfectly safe provided it is quite free from white phosphorus, which is seldom the case, especially when the heating process has not been carried far enough, or else prolonged beyond  $500^{\circ}$  F. For this reason it is advisable to store red phosphorus under water, as well as the white kind.

Making phosphorus matches is a dangerous process, which requires to be sheltered from the sun, well insulated to exclude warmth, and the different stages of the process must be kept separate. All waste must be destroyed every day. The phosphorus is generally mixed with the other ingredients at  $111^{\circ}$  F., a consistence like that of ointment being necessary to ensure the requisite fine distribution, since an irregular dissemination of the phosphorus in the composition would highly endanger the latter. The operation is still more risky when the phosphorus is employed in a dissolved condition (in carbon disulphide (*q.v.*), sulphur chloride or phosphorus trichloride), since, though the effect is intensified and phosphorus is saved, any accidental spilling or spurting of the solution will lead to danger on account of the great inflammability of the finely divided phosphorus left behind on the evaporation of the solvent. Great danger, too, attaches to the use of carbon disulphide on account of its inflammable vapour.

The match sticks are sulphured at the melting temperature of sulphur, viz.  $237^{\circ}$  F., an operation that must be carried on in a separate room from that used for working the phosphorus (igniting at  $140^{\circ}$  F.).

The danger resides less in the sulphur itself than in the treatment. Sulphur takes fire at  $500^{\circ}$  F. in the air, but when heated further in a closed vessel it boils at  $838^{\circ}$  F. When exposed to sparks while in course of treatment it readily ignites, and is liable to take fire spontaneously in

the grinding mill. Finally, in the state of floating dust it is explosive, even spontaneously so.

When ground along with carriers of oxygen, and especially those used in this process—lead peroxide, potassium chlorate, chlorates, lead chlorite, and with warm phosphorus—sulphur may give rise to violent explosions. Again, when mixed with potash and saltpetre it forms a mass that explodes on percussion; and with lampblack, freshly calcined charcoal, or with nitrous oxide, it forms spontaneously ignitable mixtures. These mixtures, however, do not occur in the manufacture of phosphorus matches.

Match sticks are sometimes coated with resin or collodion by dipping in corresponding solutions; but, as the solvents are dangerous (see *Resin*), the use of these solutions is equally so, especially when the resin has first to be melted.

Finally, after the match sticks have been successively dipped in these various ingredients—resin solution, molten sulphur, and match composition (paste)—they must be dried at a temperature not exceeding 86° F.

The dangers of phosphorus matches in use have already been partly mentioned; all that need be further said is that the matches are less dangerous than the phosphorus itself. Some protection is afforded by the other ingredients in the paste; moreover, the amount of phosphorus in a single match is very minute, being only 0.0005–0.0017 gram. (a fatal dose of phosphorus for an adult is 0.06–0.10 gram.). A million matches contain about 1–1½ lb. of phosphorus.

Commercial phosphorus matches take fire at about 113°–140°–212° F., though rarely at the first-named temperature. The minimum should be fixed at 176° F., which could easily be effected in practice.

Persulphocyanic acid (perthiocyanic acid) has been proposed as a substitute for phosphorus, its behaviour under friction and percussion rendering it particularly suitable for this purpose. It is easily obtained from the spent purifying material of gas works.

Phosphorus sesquisulphide, which does not ignite below 197½° F., is also used for the same purpose, and will be more largely employed whenever the use of phosphorus for match-making is prohibited by law. It is already largely used, in admixture with potassium chlorate, in France and Switzerland. According to the Federal law this substance must be tested for the presence of uncombined phosphorus, and be found free from the same.

Phosphorus is also used in the manufacture of phosphor bronze (copper and phosphorus treated at red heat), the preparation of phosphoric acid (by combustion in dry air or oxygen), for numerous organic preparations and as a rat poison (*Pharmaceutical Chemists*).

Phosphorus forms certain dangerous compounds with hydrogen:

A *liquid* phosphoretted hydrogen, which boils at 134½° F., ignites spontaneously in air and also in chlorine gas; with oxygen it rapidly explodes.

A *gaseous* phosphoretted hydrogen, known as phosphine, which is capable of spontaneous ignition in air, by reason of its content of the gas of liquid phosphoretted hydrogen; heated to 212° F. it takes fire, and behaves like the first-named in presence of chlorine and oxygen.

A *solid* phosphoretted hydrogen, which explodes at 320° F. or under

percussion, as also in contact with nitrous acid or nitrogen tetroxide. When exposed to damp air it decomposes, sometimes explosively.

All three compounds are met with in the laboratory only, and not in works (see *Sawdust* and *Stall Manure*).

The so-called "phosphines" are also phosphoretted hydrogens, mostly of an explosive character.

Mention must also be made of wax matches, which, being made of a composition analogous to that used for Swedish matches, are no more dangerous than the latter in this respect. On the other hand, they exhibit two highly dangerous characteristics: first, they are prone to keep alight for some time, so that a discarded wax match is more likely to cause an outbreak of fire than any other kind; and, secondly, because of the possibility of the wax of an extinguished match becoming re-kindled by contact with a still glowing match head.

These matches also take fire when trodden under foot on a hard flooring.

## CHAPTER LIX

### BENGAL LIGHTS (Coloured Fire)

IN these products the individual constituents are usually less dangerous than the mixtures. In fact, only one of them is more dangerous, namely, potassium chlorate, which must be regarded as the essential explosive element in coloured lights. The other ingredients: strontium nitrate, sulphur, lampblack, charcoal, antimony, shellac, lycopodium, sugar, stearin, barium carbonate, sodium oxalate, ultramarine, tallow, sal ammoniac, copper sulphide, and saltpetre are all less dangerous than their mixtures with the first-named. A few kinds of coloured fire are even explosive.

Even if all precautions be adopted in respect of the use of approved formulæ, the prohibition of smoking, lights, fire, heating, and the exclusion of damp, the storage of these coloured fires cannot be prolonged for more than four to five weeks without considerable risk. In that time certain changes proceed within the mass, which may become, in consequence, more or less inflammable and therefore a source of increased or diminished danger.

It is strongly advisable to mark the date of manufacture on all large parcels of coloured fire going into store, and not to allow them to get more than five weeks old. Where these products or fireworks are manufactured, no other operations may be performed, not even in the store-rooms. Moreover, the dangerous potassium chlorate must be kept separate and isolated from all other raw materials and manufactured articles. The storage of the finished products in workrooms should be prohibited.

In making coloured fires, it is not sufficient to merely mix a number of simple ingredients together, according to a set formula, since this would furnish products of low stability, that might even prove explosive,

and would certainly not stand conveyance by rail. Consequently, certain points must be borne in mind, in order to obtain safe and transportable finished products. This condition entails the use of chemically pure ingredients, guaranteed as such by the seller. Fineness of division is also essential, and, as the ingredients are generally purchased in a somewhat coarser condition, owing to the occurrence of balling in the drying process, they must be powdered anew before use. This operation is open to serious objection in the case of potassium chlorate, and must be performed on small quantities at a time, kept damp and worked with soft tools (wood). Potassium chlorate must never be powdered in association with other substances, and only in special apparatus that is used for no other purpose.

The operation of pulverising the other ingredients is attended with little or no danger, but they must all be treated separately. Above everything, there must be no attempt to save time and labour by effecting the pulverising and mixing at one operation; this would be in the highest degree incautious.

As a third precaution, the ingredients must be thoroughly dry before they are mixed; for, like many others, these substances are somewhat hygroscopic, and the absorbed moisture militates against their intimate admixture.

Drying must never be postponed until after mixing, but each substance must be dried beforehand, separately, and indeed before the final pulverisation. To dry the mixed ingredients is as dangerous as to triturate them.

The finished products will stand a fair amount of heat, since, according to W. Thörner, they may be raised to 278° and 392° F. before taking fire; but as all factories are not fitted with drying appliances that enable the temperature to be so accurately controlled as is here essential, it therefore becomes necessary to dry the ingredients separately. The temperature must not exceed 212° F., but, on the other hand, the period of drying can be the more prolonged on that account.

After the pure materials have been dried and ground, they are mixed. This operation is also attended with no small risk; if large quantities are in question, the mixing is best performed out of doors, but only in dry weather; otherwise, in lightly constructed sheds made as fireproof as possible.

In mixing by hand, all hard or metallic tools must be avoided, as also any violent shocks, blows, or friction. A soft, felty underlay must be provided, and the floor must be covered with soft material. The ingredients must not be mixed so long as they are still warm from the drying room.

For mixing large quantities a mixing cylinder should be employed, and one too that will enable the operation to be properly performed, since thorough incorporation is the only way of obtaining a product that will burn satisfactorily. The cylinder must be so arranged that the ingredients in the corners are mixed as uniformly as the rest. The work within the cylinder must be confined strictly to mixing; on no account should there be any grinding there. All cracks or interstices in which traces of the ingredients could collect must be abolished; and the formation of sparks must be rendered impossible.

Practical experience has shown that spontaneous explosion may occur

in handling the finished products with wooden shovels, especially when the materials have been warmed by the sun or other source of heat, or when they have formed a hard crust. In the latter event, it is impossible to avoid some friction, which will be especially dangerous to old mixtures.

Great caution in all respects must be observed in the manufacture of fuses (from potassium chlorate and antimony sulphide).

Under all circumstances, the whole of the other ingredients must be mixed before adding the potassium chlorate, this, when required at all, being mixed in last. It should, moreover, be emphasised that even the preliminary mixing of the potassium chlorate with sugar, flour, sulphur, antimony, lycopodium, colophony, and lampblack, *i.e.* apparently innocuous ingredients, is a very dangerous procedure (see *Chlorates*).

According to the reports of pyrotechnists, an addition of lycopodium (the spores of a kind of club moss) decreases the explosibility of firework charges; but W. Thörner is of a contrary opinion.

Firework factories are subject to numerous Government regulations; but it should be stated that coloured fires and Bengal lights are made in other establishments (drug stores, &c.), which are far from complying with the terms of these regulations. For festive occasions, illuminations, and the like, large quantities of coloured fire are made to order in a short time; and under these circumstances it is probable that the necessary precautions are not always carefully observed. In this connection, the following observations may be made:—

All waste must be rendered harmless by immersion in water. The mixtures must be sheltered from the sun. While the mixtures are being prepared, all other operations must be suspended, particularly any work entailing the use of sulphuric acid. Care must be taken to remove the usually large stocks of alcohol, ether, benzol, and similar liquids; and great precaution with regard to lighting and heating must be taken while the manufacture of coloured fires is in progress.

In the author's opinion, far greater danger attaches to such drug stores and similar establishments, where coloured fires are produced quickly and in large quantities on special occasions, than to premises where these articles are produced regularly on a large scale all the year round, and are rendered suitable therefor by compliance with Government regulations.

The following table records the results of experiments conducted by Thörner in connection with mixtures for coloured fires:—

Ingredients (All the mixtures contained 8-40 per cent. of potassium chlorate)	Colour of the Flame	The Mixture gave		The Mixture ignited	
		When strongly triturated with a pestle	Explosion when hammered on the anvil	When heated on an iron plate. Minutes	When heated in an air-bath. At °F.
I. { Strontium nitrate . . . } Sulphur . . . . . Lampblack . . . . .	red	no ignition	slight	3.4	392°
II. No. I. plus Antimony sulphide . . . . .	red	slight explosion	strong	3.1	{ 345°; after a month 311°
III. { Strontium nitrate . . . } Sulphur . . . . . Antimony . . . . .	red	explosion	strong	2.0	332½°
IV. { Strontium nitrate . . . } Shellac . . . . .	orange	no ignition	slight	2.8	392°
V. { Saltpetre, sugar . . . } Stearin . . . . . Barium carbonate . . . }	white	no ignition	strong	2.9	{ 284°; after a month 392°
VI. { Saltpetre . . . . . } Sodium oxalate . . . } Shellac . . . . .	yellow	no ignition	slight	5.0	392°
VII. { Barium nitrate . . . } Sugar . . . . .	green	no ignition	slight	2.75	278½°
VIII. { Sulphur . . . . . } Antimony . . . . . Ultramarine (copper) . }	blue	no ignition	strong	3.0	{ 375¾°; after a month 302°
IX. { Copper sulphide . . . } Sal ammoniac . . . . } Sugar, tallow . . . . }	blue	slight explosion	strong	2.0	336¼°
X. { Strontium nitrate . . . } Copper sulphide . . . } Sulphur . . . . . Sal ammoniac, sugar . }	violet	no ignition	slight	2.2	302°

From these results it is evident that the coloured fire preparations are more or less readily inflammable and explosive. If they do not ignite under friction, they will do so on percussion. Moreover, the ignition point may sink after the lapse of a month (by 34¼°-73¾° F.), or in some cases rise (V., by 108° F.).

The ignition point is lower when rapid heating is practised, but considerably higher when the heat is applied slowly. Hence, in the event

of an outbreak of fire, the risk of ignition and explosion is far more acute in large stocks than when gradual decomposition ensues from protracted exposure to the moderate heat of a stove or light. In the latter case, the destruction is confined to the materials used in making the lights, while in the former other objects are also involved.

Instances of spontaneous ignition are attributable solely to the use of impure ingredients, or to accidents, like a fall or a shock.

It is evident, also, that all the regulations laid down for dangerous establishments must be carefully observed in premises where coloured fires are made or stored ; and that the work cannot be carried on along with other operations in laboratories or drug stores without danger to the latter.

# APPENDIX

## TABLE I.—DANGEROUS SUBSTANCES

List of the principal substances, mixtures, and gases liable to spontaneous ignition, explosion, and high fire risk, with particulars of their most dangerous reactions. Information is also included as to which substances should not be stored together, and may only be brought into mutual contact under special precautions. For other particulars see text.

### ABBREVIATIONS :

- g.* Gaseous substance.
- l.* Liquid.
- s. ex.* Spontaneously explosive.
- ex.* Explosive (in contact with flame or sparks).
- s. inf.* Spontaneously inflammable.
- inf.* Inflammable (by contact with flame or sparks).
- s. gl.* Capable of glowing spontaneously.
- gl.* Becoming red hot.

Substances not marked *g.* or *l.* are solid.

Acetic acid (glacial), <i>l.</i>	<i>ex.</i> with chromic acid, sodium peroxide, or nitric acid. <i>inf.</i> when warmed with ammonia; boiling acetic acid yields combustible vapours.
Acetone, <i>l.</i>	<i>ex.</i> as vapour with air; with hydrogen peroxide.
Acetone peroxide	<i>ex.</i> percussion.
Acetylene, <i>g.</i>	<i>s. ex.</i> with chlorine in the sun. At 480° C. when containing chlorine. <i>s. inf.</i> when contained in chlorine; with phosphoretted hydrogen. <i>ex.</i> with air or oxygen. By percussion, friction, flame, or spark, when under a pressure of 2 atmospheres and over. From any cause when liquid. <i>s. ex.</i> as a salt of Cu, Ag, or Hg, prepared by the wet method. <i>ex.</i> the same salts (by the dry method), by percussion, or at 120° C.
Acetyl peroxide, <i>l.</i>	<i>ex.</i> at 100° C.
Air, <i>g.</i>	<i>ex.</i> with organic substances when liquefied.
Alcohol, <i>l.</i>	<i>s. ex.</i> with permanganic acid or perchloric acid. <i>ex.</i> (as vapour) with air, but only when strongly warmed. <i>ex.</i> with silver nitrate, warmed with mercury (fulminate compound), with potassium permanganate and sulphuric acid.
Alum	<i>s. inf.</i> with freshly calcined charcoal.
Aluminium triethyl, <i>l.</i>	<i>s. inf.</i> in air.
Aluminium trimethyl, <i>l.</i>	<i>s. inf.</i> in air.
Aluminium tripropyl, <i>l.</i>	<i>s. ex.</i> in air.
Amber (artificial)	<i>ex.</i> See <i>Celluloid</i> .
Ammonia, <i>l.</i>	<i>s. ex.</i> on introducing chlorine gas (nitrogen chloride); when mixed with iodine. <i>ex.</i> with gold chloride (gold fulminate).

Ammonium nitrate . . .	inf. when warmed with acetic acid.
Ammonium nitrite . . .	ex. at 70° C, or by percussion.
Ammonium permanganate . . .	ex. by percussion.
Amyl nitrite, Iso-, l. . .	ex. when warmed as vapour.
Antimony triethyl, l. . .	s. inf. See <i>Triethylstibine</i> .
Antimony trimethyl, l. . .	s. inf. See <i>Trimethylstibine</i> .
Antimony sulphide . . .	ex. when triturated or struck in presence of potassium chlorate.
Arsenic diethyl, l. . .	s. inf. in air.
Arsenic dimethyl, l. . .	s. inf. in air.
Azoimide, l. . .	s. ex. on the slightest inducement, at room temperature. ex. even when dissolved in water; with mercury or silver.
Bengal Lights . . .	s. ex. by spontaneous decomposition, in an impure state. ex. by friction or percussion, according to composition. inf. at 130°–200° C, according to composition.
Benzol, l. . .	s. ex. with permanganic acid; by electric sparks (with air). ex. as vapour with air; with potassium permanganate and sulphuric acid; with perchloric acid.
Beryllium ethyl, l. . .	s. inf. in air.
Bismuth ethylchloride . . .	s. inf. in air.
Bismuth triethyl, l. . .	s. inf. in air.
Blasting gelatine . . .	ex. at 150° C. inf. at 270° C.
Bleaching powder . . .	ex. in a frozen state; by percussion. ex. when tightly packed and exposed to heat or sunlight.
Boron, amorphous . . .	inf. at 300° C.
Boron triethyl, l. . .	s. ex. with oxygen. s. inf. in air.
Boron trimethyl, g. . .	s. ex. with oxygen or suddenly mixed with air. s. inf. in air.
Bromacetylene, g. . .	s. inf. in air.
Bromates, . . .	behave like chlorates, but less violently.
Bromine, l. . .	See <i>Ethyl phosphine</i> , <i>Lead triethyl</i> , <i>Sodium carbide</i> .
Bronze powders . . .	ex. with carriers of oxygen, peroxides; with water, steam (oxyhydrogen gas). ex. when floating as dust by flame, spark, or electric sparks.
Cacodyl dioxide, l. . .	s. inf. in air.
Cacodyl sulphide, l. . .	s. inf. in air.
Calcium carbide . . .	gl. with water in small amount (see <i>Acetylene</i> ).
Calcium hypochlorite . . .	See <i>Bleaching powder</i> .
Calcium nitride . . .	s. inf. in air.
Carbides . . .	See the various carbides.
Carbon disulphide, l. . .	s. ex. when the vapours are warmed to 100°–150° C; especially in presence of dust. ex. when the vapours are mixed with air or oxygen; when the vapours are compressed. ex. with hyponitrous acid; triturated or pounded with potassium or sodium. inf. with per acids, perchloric acid, permanganic acid; with potassium permanganate and sulphuric acid; when lightly touched with a glass rod dipped in ether.
Carbon monoxide, g. . .	ex. by contact with flame when mixed with air; with damp oxygen; when combined with potassium.
Carbon oxysulphide, g. . .	ex. with glowing bodies, in admixture with air or oxygen.
Celloidin, l. . .	far less dangerous than ether ( <i>q.v.</i> ).
Celluloid . . .	ex. by percussion; at 140° C; as dust, by the smallest spark. inf. by sparks, prolonged heat, radiant heat.
Cellulose nitrate . . .	See <i>Guncotton</i> , <i>Collodion</i> , <i>Celloidin</i> , <i>Collodion wool</i> .

- Charcoal powder . . . . s. inf. when freshly calcined and exposed to air; freshly ground and tightly packed; with nitrogen protoxide. ex. by the smallest spark when floating in clouds; with perchloric acid.
- Chloracetylene, l. . . . s. ex. on standing.
- Chlorates . . . . . ex. on slight friction, percussion, shock, and when crushed.  
ex. by percussion when mixed with organic substances (sugar, meal, shellac, &c.); with charcoal, sulphur, or manganese dioxide (when warmed).  
ex. with sulphuric acid (chlorine tetroxide); with potassium cyanide; with thiocyanates; with lead thiocyanate; with phosphorus, or antimony sulphide.
- Chloric acid, l. . . . . inf. with organic substances.
- Chlorine, g. . . . . s. ex. with hydrogen, methane, acetylene, ethylene, in sunlight and with artificial light, with hydrogen silicide.  
ex. when passed into ammonia (nitrogen chloride); with methyl ether; with ethyl phosphine.  
s. inf. with phosphorus, bismuth, arsenic, antimony, gold leaf, bronze powder, iron, and many other metals in a finely divided state; with sodium carbide.  
s. inf. with organic substances that have been dipped in oil of turpentine; with phosphoretted hydrogen.
- Chlorine heptoxide, l. . . See *Perchloric acid*.
- Chlorine peroxide, g. . . s. ex. in contact with organic matter like cork or caoutchouc.
- Chlorine tetroxide, g. . . See *Hypochlorous anhydride*.
- Cholacrol, l. . . . . ex. at 100° C.
- Chromates . . . . . inf. on contact with sulphuric acid; with phosphorus and organic matters (oils, petroleum, ether, coal gas).  
ex. with acetic acid or alcohol.
- Chromic acid . . . . . inf. with organic substances.
- Chromium protoxide . . s. gl. when triturated in a mortar.  
inf. when gently warmed.
- Cobalt powder . . . . . s. inf. in air.
- Collodion, l. . . . . nearly as dangerous as ether (*q.v.*),
- Collodion wool . . . . inf. at 150° C.  
ex. at 186° C.
- Colloidin . . . . . like collodion wool, but less dangerous.
- Copper acetylene . . . ex. see *Acetylene*.
- Copper tetrazol . . . . ex. when warmed.
- Cyclopentanes, l. . . . ex. with strong sulphuric acid or nitric acid.
- Diacetylene, g. . . . . s. ex. with damp silver salts.
- Diacetylene dicarbonic acid . . ex. at 177° C.
- Diazoamido benzol . . . . ex. when warmed.
- Diazoamido naphthalene . . ex. at 100° C.
- Diazobenzoic nitrate . . . ex. when warmed.
- Diazobenzol anilide . . . ex. at 81° C.; by percussion.
- Diazobenzol chloride . . . ex. when warmed; by percussion.
- Diazobenzolimid . . . . ex. when warmed; by slight shock.
- Diazobenzol nitrate . . . ex. when warmed; by percussion; more violently than mercury fulminate.
- Diazobenzol sulphate . . . ex. at 100° C., or by a sharp blow.
- Diethylphosphine, l. . . s. inf. in air.
- Di-iododiacetylene . . . ex. when warmed.
- Dimercuric ammonium oxide . . . . . ex. when warmed.
- Dimethylphosphine, l. . . s. inf. in air.
- Dinitronaphthol salts . . . ex. when warmed.
- Dipropargyl, l. . . . . ex. when warmed; with copper or silver salts.
- Dynamite . . . . . s. ex. in a frozen state; at 8° C.  
ex. when violently heated (by exploding mercury fulminate).

- Ether, l. . . . . s. ex. with oxygen, ozone, oil of turpentine, permanganic acid or perchloric acid.  
ex. in the state of vapour with air; with potassium permanganate and sulphuric acid.  
ex. when become acid, in sunlight, with formation of vinyl alcohol.
- Ethereal oils, l. . . . . inf. with iodine (detonating), fuming nitric acid. See *Oil of Turpentine*.
- Ethylene, g. . . . . s. ex. with twice its volume of chlorine in the sunlight.  
ex. with a 15-fold volume of air or 3-fold volume of oxygen.
- Ethyl nitrate, l. . . . . ex. at 87° C.
- Ethyl nitrite, l. . . . . s. ex. by spontaneous decomposition (at 90° C) during storage; at 75° C. with fat or organic matter.
- Ethyl phosphine, l. . . . . ex. with bromine, chlorine, or fuming nitric acid,
- Firedamp, g. . . . . See *Methane*.
- Firework charges . . . . . Like Bengal lights.
- Fulminates . . . . . ex. like gold fulminate.
- Gas, coal-, g. . . . . ex. mixed with air; at 647° C.; with potassium permanganate and sulphuric acid.  
inf. in contact with spongy platinum and platinum wire.
- Gasoline, l. . . . . ex. as vapour mixed with air.
- Glycerin . . . . . See *Potassium permanganate*.
- Gold carbide . . . . . ex. by percussion or rapid heating.
- Gold fulminate . . . . . ex. when warmed; by percussion, friction, shock, electric sparks, or strong acids.
- Gold nitrate . . . . . ex. when warmed with alcohol (fulminates).
- Guncotton . . . . . ex. when suddenly warmed; warmed in closed vessels; at 139° C.; by friction, shock, pressure, when strongly dried.  
s. ex. when impure; too strongly dried; when pressed too tightly and heated to 186° C.
- Gunpowder . . . . . ex. by heating in closed vessels.  
inf. at 270° C.; by sparks, glowing bodies, shock, friction, percussion.  
s. ex. when repeatedly warmed and cooled alternately; when hard and encrusted masses of the powder are broken down.
- Hydrogen, g. . . . . s. ex. with chlorine in the sun or artificial light; with oxygen or air in presence of spongy platinum or finely powdered glass and other powders (carbon) with an attraction for oxygen.  
ex. with air, oxygen, nitrogen protoxide, or substances yielding up oxygen.
- Hydrogen peroxide, l. . . . . s. ex. with acetone, dust, or metallic dust.  
ex. (in the concentrated or crystalline state) by warmth or brisk agitation; with the gases or vapours of readily inflammable substances (ether, benzol, &c.).  
s. inf. (in the crystalline state) on contact with: peroxides, carriers of oxygen, manganese dioxide, lead powder, wool, fibres, damp or porous substances, or mixtures of carbon with metal powders and manganese dioxide.
- Hydrogen silicide, g. . . . . ex. with air or chlorine gas; with hydrogen.  
s. inf. when impure.
- Hypochlorous anhydride, g. . . . . ex. with sulphur, phosphorus, or organic substances; at 60° C.
- Hyponitrites . . . . . ex. by friction.
- Hyponitrous acid, l. . . . . ex. with carbon disulphide.
- Igniting pellets . . . . . s. ex. when exposed to the sun.
- Indium protoxide . . . . . gl. in air.
- Iodates . . . . . behave like chlorates, but less energetically.
- Iodine . . . . . s. ex. when suffused with ammonia.  
ex. with oil of turpentine or lead triethyl.  
inf. with ethereal oils (*q.v.*).

Iodobenzol . . . . .	ex. at 230° C.
Iodosobenzol . . . . .	ex. at 210° C.
Iodosotoluol . . . . .	ex. at 178° C.
Iodotoluol . . . . .	ex. at 228° C. (para-); the ortho- at 210° C.
Iodovasogene . . . . .	ex. when mixed with ammoniacal substances (nitrogen iodide).
Iron . . . . .	ex. on contact with water or steam whilst glowing. s. ex. in the form of freshly prepared fine powder on exposure to air, or mixed with sulphur.
Iron carbide . . . . .	inf. at 150° C.
Iron sulphide . . . . .	s. inf. in contact with moist organic, carbonaceous substances.
Lampblack . . . . .	ex. as dust in closed rooms. s. inf. on exposure to air in a freshly prepared state; with sulphur, metallic sulphides, oils, or fats; from petroleum refinery stills.
Lead chlorite . . . . .	s. inf. when mixed with sulphur. ex. rubbed with sulphur or metallic sulphides; warmed to 100° C.
Lead oxide (red) . . . . .	ex. when dusted as paint powder, but only by direct contact with flame.
Lead peroxide . . . . .	s. inf. with sulphur, or when spread out with amorphous phosphorus (may also be ex.). gl. with sulphur dioxide.
Lead picrate . . . . .	s. inf. as dye in silk or fabrics.
Lead triethyl, l. . . . .	ex. with iodine or bromine.
Lignite dust . . . . .	s. inf. when heated to 150° C.
Ligroin, l. . . . .	ex. as vapour mixed with air.
Lime, quick- . . . . .	s. gl. on contact with water, up to 800° C.; then ignites organic matter.
Linde's air, g. . . . .	See <i>Air</i> .
Magnesium ethyl. . . . .	s. inf. in air.
Magnesium methyl . . . . .	s. inf. in air.
Manganese heptoxide . . . . .	s. inf. in contact with organic matter.
Manganese linolate . . . . .	s. inf. when freshly precipitated and exposed to the air.
Manganous hydrate . . . . .	s. inf. in contact with air after drying in hydrogen gas.
Mannite hexanitrite. . . . .	ex. by percussion.
Mercury fulminate . . . . .	Like <i>Gold fulminate</i> .
Mercury nitrate . . . . .	See <i>Gold nitrate</i> .
Mercury nitride . . . . .	ex. when rubbed, warmed, or struck; at over 130° C.
Methane, g. . . . .	s. ex. with chlorine in the sun. ex. with air or oxygen; at 650° C.
Methyl alcohol, l. . . . .	ex. as vapour mixed with air.
Methyl ether, g. . . . .	ex. with chlorine gas (methyl oxide).
Methyl nitrate, l. . . . .	ex. by percussion, or on warming.
Methyl nitrite, l. . . . .	ex. at 66° C.; by percussion.
Minium . . . . .	See <i>Lead oxide (red)</i> .
Naphthoquinone chlorimide . . . . .	ex. at 130° C.
Nickel carbon monoxide, l. . . . .	ex. at 60° C.
Nitrates . . . . .	ex. (gold-, silver-, or mercury nitrate) when warmed with alcohol (fulminates). inf. at 500°-850° C. See <i>Saltpetre</i> .
Nitric acid (strong), l. (Nitrating liquid) . . . . .	ex. with sulphuretted hydrogen, when the acid is fuming. inf. with organic substances (straw, wood, paper, textiles, &c.); with oil of turpentine, ethereal oils, or ethyl phosphine.
Nitric anhydride . . . . .	s. ex. on prolonged storage in the warm.
Nitrites . . . . .	Like <i>Sodium nitrite</i> .
Nitrocellulose . . . . .	See <i>Cellulose nitrate</i> .
Nitro-compounds . . . . .	s. ex. (see the various nitro-compounds and nitrates) when stored in an impure state.

Nitroerythrite . . . . .	ex. by percussion. inf. when warmed.
Nitroform . . . . .	ex. when warmed.
Nitrogen bromide, l. . . . .	ex. on the slightest provocation; as percussion, vibration, friction; otherwise like nitrogen chloride but less violently.
Nitrogen chloride, l. . . . .	s. ex. on the slightest provocation; in sunlight or magnesium light; by sound waves (concert). ex. at 90° C.; in contact with turpentine, caoutchouc, fat, oil, train oil, arsenic, phosphorus, selenium, potassium, ammonia.
Nitrogen fluoride, l. . . . .	s. ex. on slightest provocation; in the sun. ex. at 90° C.; in contact with oil of turpentine, caoutchouc, oil, train oil, fat, arsenic, antimony, phosphorus, selenium, potassium, ammonia.
Nitrogen iodide . . . . .	s. ex. on slightest provocation; on exposure to sunlight in a damp state.
Nitrogen peroxide, g. . . . . (Nitric oxide)	ex. in contact with any inflammable gas or vapour.
Nitrogen protoxide, g. . . . . (Nitrous oxide)	ex. with hydrogen gas. inf. in contact with warmed substances, like phosphorus, sulphur, or carbon.
Nitrogen sulphide . . . . .	ex. by shock or friction. inf. by melting; at 179° C.
Nitroglycerin, l. . . . . (Nobel's Blasting Oil)	s. ex. when frozen and warmed. ex. by percussion, shock, warming; at 257° C.
Nitromannite . . . . .	ex. by percussion; at 120° C. s. ex. by spontaneous decomposition on prolonged storage.
Nitromethane, l. . . . .	ex. in combination with heavy metals.
Nitronaphthols . . . . .	ex. when warmed.
Nitroparaffin, l. . . . .	Like <i>Nitromethane</i> .
Nitrophenylacetylene . . . . .	ex. in combination with metals.
Nitrosaccharose . . . . .	ex. by percussion.
Nitrosophenol . . . . .	ex. when warmed; at 120° C.
Oils, ethereal, l. . . . .	See <i>Ethereal oils</i> .
Oils, fatty, l. . . . .	s. inf. when distributed in fibres and fabrics.
Organic substances, l. . . . .	Of the numerous substances that can be ignited or exploded by organic substances, or dust, mention may be made of the following: s. ex. chlorine peroxide. ex. chlorates, liquid air, sodium peroxide, picric acid, liquid ozone and oxygen, hydrogen peroxide, hypochlorous anhydride. s. inf. chlorine, when the organic substances are steeped with oil of turpentine or ethereal oils; manganese heptoxide, iron sulphide. inf. chromates (with sulphuric acid), chromic acid, chloric acid, lime (quick and slaked), strong nitric acid, nitrating liquid, carriers of oxygen, permanganates (with friction).
Osotriazol, l. . . . .	ex. when warmed.
Oxygen, carriers of . . . . .	ex. with fine metallic powders (bronzes). inf. (after treatment with sulphuric acid) with organic substances, mineral oils, ethereal oils, oil of turpentine, coal gas, or vapours of readily inflammable liquids.
Oxygen, liquid, l. . . . .	ex. with organic substances which are gently warmed. See <i>Carriers of oxygen</i> .
Oxyhydrogen gas, g. . . . .	s. ex. at 700° C. (or 674° C. according to A. Mitscherlich). ex. by flame, electric sparks, spongy platinum, metallic powders.
Oxypicric acid . . . . .	Like <i>Styphnic acid</i> .
Ozone, liquid, l. . . . .	s. ex. with combustible gases and vapours; on distillation for the separation of oxygen. ex. in contact with organic matter.

Palmitic acid . . . . .	ex. at 320° C.
Perchloric acid, l. . . . .	s. ex. when stored 2-3 days. ex. in contact with flame, paper, carbon, ether, carbon disulphide, benzol, alcohol, or inflammable gases.
Permanganates . . . . .	ex. when treated with sulphuric acid and brought into contact with: alcohol, ether, benzol, carbon disulphide, petroleum, oils (ethereal), inflammable gases, or organic substances.
Permanganic acid, l. . . . .	ex. at 65° C.; otherwise like perchloric acid.
Permanganic anhydride . . . . .	See <i>Manganese heptoxide</i> .
Petroleum, l. . . . .	ex. when heated in closed lamps. s. inf. in contact with potassium permanganate and sulphuric acid.
Petroleum ether, l. . . . .	ex. mixed with air, as vapour. s. inf. with permanganic acid; with potassium permanganate and sulphuric acid.
Phosphine . . . . . (Phosphamine)	s. inf. phosphoretted hydrogen compounds, which, by reason of the presence of that constituent are spontaneously inflammable in air.
Phosphoretted hydrogen, l. . . . .	s. ex. with oxygen gas. s. inf. in air; with chlorine.
Phosphoretted hydrogen, g. . . . .	s. ex. with oxygen in a partial vacuum. s. inf. in air; with chlorine; at 100° C.
Phosphoretted hydrogen . . . . .	s. inf. with nitrous acid; with nitrogen tetroxide; by percussion; at 160° C.
Phosphorus (red) . . . . .	ex. with potassium chlorate or chromate (when warmed), saltpetre, lead peroxide (when rubbed or warmed). inf. in larger lumps, only in presence of white phosphorus.
Phosphorus (white) . . . . .	s. ex. in contact with carriers of oxygen, peroxides, peracids, sulphur. s. inf. in large pieces (1 lb.); when in a very finely divided state. inf. on slight friction; with chlorine gas; at 60° C.; with nitrogen protoxide.
Phosphorus sesquisulphide . . . . .	inf. at 92° C.
Picraminates . . . . .	ex. when warmed.
Picrates . . . . .	ex. by shock, percussion, drying, warming, burning substances, friction; see text.
Picric acid . . . . .	ex. when contaminated by picrates or adulterated with organic substances; with strong nitric acid; by sudden warming, or by gradual warming in closed vessels.
Platinum (spongy) . . . . .	gl. on exposure to a current of coal gas, hydrogen, vapour of ether or wood spirit (the gases or vapours are ignited).
Potassium . . . . .	s. ex. when treated with water. ex. with carbon disulphide; by pressure or friction. inf. when gently warmed in air, or treated with water or damp substances.
Potassium carbide . . . . .	Like <i>Sodium carbide</i> .
Potassium chlorate . . . . .	See <i>Chlorates</i> .
Potassium cyanide . . . . .	ex. with chlorates or potassium nitrite; at 450° C.
Potassium hydride . . . . .	s. inf. in air.
Potassium nitrite . . . . .	ex. with potassium cyanide when heated to 400° C.; when mixed with ammonium salts.
Potassium nitrocyanide . . . . .	ex. at 400° C.
Potassium peroxide . . . . .	ex. like sodium peroxide.
Potassium sulphide . . . . .	s. inf. when exposed to the air in a freshly prepared state; when warmed with carbon.
Propargyl alcohol . . . . .	ex. when warmed with silver or copper salts.
Propargylic acid . . . . .	ex. when warmed with silver or copper salts.
Pyrophores . . . . .	s. inf. See <i>Potassium sulphide</i> .
Pyroxylin . . . . .	See <i>Guncotton</i> .
Rubidium . . . . .	s. inf. when treated with water.

Ruthenium tetroxide . . .	ex. at 108° C.
Saltpetre (see <i>Nitrates</i> ) . .	inf. When used for impregnating textiles renders them highly inflammable. inf. at 500°-800° C. with powerful detonation. ex. when mixed with potash and sulphur; by percussion and warming; when thrown on to glowing carbon.
Selenium . . . . .	gl. when merely warmed to 100° C. the temperature rises, by spontaneous heating, to over 200° C.
Silicon chloroform, l. . . .	ex. when gently warmed in air.
Silver . . . . .	s. ex. with acetylene. ex. when rapidly warmed with oxalic acid.
Silver fulminate . . . . .	ex. like gold fulminate, but stronger, and even in a damp state.
Silver nitrate . . . . .	See <i>Gold nitrate</i> .
Silver nitride . . . . .	ex. by percussion or warming.
Silver oxalate . . . . .	ex. when rapidly warmed.
Silver tetrazol . . . . .	ex. when warmed.
Soda residues . . . . .	s. gl. when stored in great heaps; by calcium sulphide.
Sodium . . . . .	Like potassium but weaker.
Sodium carbide . . . . .	gl. in chlorine gas, carbon dioxide, or sulphur-dioxide. ex. with bromine vapour; with water.
Sodium hydride (crystals) .	s. inf. when moistened with water.
Sodium nitrate . . . . .	Like <i>Potassium nitrate</i> .
Sodium nitrite . . . . .	See <i>Potassium nitrite</i> .
Sodium peroxide . . . . .	s. inf. with water and aniline, or benzol, or ether. ex. or merely inf. with damp aluminium bronze, oil of bitter almonds, phosphorus, charcoal, glycerin, glacial acetic acid, or inflammable substances like wood, paper, or fibres.
Styphnates . . . . .	ex. when warmed.
Styphnic acid . . . . .	ex. when warmed.
Succinyl peroxide . . . . .	ex. on the slightest touch or when warmed.
Sulphur . . . . .	ex. when rubbed down as dust with lead peroxide, chlorates, lead chlorite, warm phosphorus; when warmed or struck in admixture with saltpetre and potash. s. inf. with lampblack; with freshly calcined charcoal; with nitrogen protoxide.
Sulphuretted hydrogen, g.	ex. with fuming nitric acid. s. inf. with the peroxides of lead or bismuth, or permanganic acid; with metallic dust, bronze powders (aluminium, zinc, or bismuth).
Tellurium nitride . . . . .	ex. by percussion; at 200° C.
Tetracetylenedicarbonic acid . . . . .	ex. on the least provocation.
Thiocyanates . . . . .	ex. when rubbed with chlorates or mixed with saltpetre; at 400° C.
Triethylbismuthine, l. . . .	ex. at 150° C.
Triethylphosphine, l. . . .	inf. with oxygen, chlorine, or acids. ex. with oxygen.
Triethylstibine, l. . . . .	s. inf. in air.
Trimethylstibine, l. . . . .	s. inf. in air.
Trinitroacetoneitrile . . . .	ex. at 200° C.
Trinitrophenolglucin . . . .	ex. at 158° C.
Trioxime . . . . .	ex. at 155° C.
Turpentine oil, l. . . . .	ex. with iodine, ether, nitrogen chloride, or nitrogen fluoride. inf. with strong nitric acid, nitrating liquid; in chlorine gas; with carriers of oxygen that have been moistened with sulphuric acid.
Uranium carbide . . . . .	ex. by percussion, strong friction; the explosion is attended by ignition.
Vinyl alcohol, l. . . . .	ex. on the slightest warmth or other provocation.

Water, l. . . . .	ex. in contact with glowing metals (oxyhydrogen gas); with potassium, sodium, or rubidium; with bronze powders (aluminium).
	gl. in contact with calcium carbide or quicklime.
Xyloidin. . . . .	ex. when warmed (nitrocompounds of starch).
Zinc dust . . . . .	inf. and even ex. in moist air; when treated with water; with acids (oxyhydrogen gas).
Zinc ethyl, l. . . . .	s. inf. in air.
Zinc isoamyl, l. . . . .	s. inf. in air.
Zinc isobutyl, l. . . . .	s. inf. in air.
Zinc methyl, l. . . . .	s. inf. in air.
Zinc propyl, l. . . . .	s. inf. in air.
Zirconium, amorphous. . . . .	s. inf. in air when freshly prepared.

TABLE II.—WORKING TEMPERATURES

The following particulars regarding the temperatures employed in various operations and works cannot lay any claim to completeness; they are merely designed to give a general idea of the temperatures customary in different operations, and thus enable an opinion to be formed on the general fire risk, so far as this can be done on the basis of temperatures. That the latter are not the sole criterion, need not be said; premises working with temperatures of 1000°–2000° C. are often safer from fire than others where the temperature does not exceed 100°–200° C. Hence the table will serve more for instruction, information, and comparison in connection with various branches of the chemico-technical industry.

The temperatures are naturally subject to considerable fluctuation, rising or falling in accordance with the technical arrangement of the premises, the materials and the processes employed. When the establishment is arranged on normal lines, not only will any desired high temperature be more uniformly maintained, but the dangers resulting from such high temperatures will be more securely averted than where the arrangements are of a less perfect character.

For this reason high temperatures need not be a source of apprehension, provided the plant is well arranged, though lower temperatures may entail greater danger in defective establishments.

To avoid repetition, a number of temperatures given in the text have been omitted; hence the latter should be consulted as well.

### The Working of Ores and Metals.

Temperature Degs. C.	
700–950 . . . . .	Ore roasting.
580–900 . . . . .	Roasting pyrites, blende.
500 . . . . .	Roasting alum shale, for alum.
500 . . . . .	Roasting bauxite for sodium aluminate.
400–500 . . . . .	Recovery of sulphur from pyrites.
1400–1613 . . . . .	Formation of slag in blast-furnaces.
400–800 . . . . .	Heating the blast in blast-furnaces.
2100 . . . . .	Making wrought iron in the Bessemer retort.
1300 . . . . .	Puddling furnace.
1500 . . . . .	Siemens-Martin regenerator.
1930 . . . . .	At the twyers of the blast-furnace.
650–870 . . . . .	Roasting copper ores for the recovery of silver, according to Ziervogel.
1200–1400 . . . . .	Welding temperature.
950–1000 . . . . .	Smithy temperature.
1800 . . . . .	Fusing point of platinum.
1300 . . . . .	Spongy platinum from ammonium-platinum chloride.
500 . . . . .	Recovery of mercury from cinnabar.
230–260 . . . . .	Amalgamation of zinc.
525–600 . . . . .	Formation of anti-corrosive layer of iron protoperoxide on iron.

Temperature  
Degs. C.

600-700 . . . . .	Fire-gilding metals.
430-500 . . . . .	Galvanising metals.
850 . . . . .	Tinning glowing metal.
235 . . . . .	Tinning metals in molten tin.
334 . . . . .	Coating metals with lead.
15-20 . . . . .	Temperature of galvanic bath for nickel-, gold-, and silver-plating.
1320 . . . . .	Metal at blast-furnace tap-hole.
1700 . . . . .	Slag temperature in the converter.
1500 . . . . .	Temperature of converter gases.
250-270 . . . . .	Drying nickel plating, to prevent peeling.
350-1000 . . . . .	Hardening metal tools.

### Annealing Temperatures of Metals.

220 . . . . .	Pale yellow.
230 . . . . .	Straw yellow.
260 . . . . .	Brown.
277 . . . . .	Purple.
288 . . . . .	Pale blue.
293 . . . . .	Dark blue.
316 . . . . .	Blue black.
3500 . . . . .	Electric arc in the carbide furnace.
2800 . . . . .	The Goldschmidt thermite process with aluminium powder.
1000-2000 . . . . .	Blowpipe and soldering lamp temperatures.
1200-1500 . . . . .	Temperature of laboratory electric furnace.

### Coal, Petroleum, and Tar Industries.

70-75 . . . . .	Drying lignite.
75-90 . . . . .	Drying materials for briquettes.
1000 . . . . .	Hot-air temperature for coke ovens.
600-700 . . . . .	Effluent gases from coke ovens.
400-500 . . . . .	Briquette making.
400-500 . . . . .	Briquetting ores.
250-300 . . . . .	Charring peat.
220 . . . . .	Heating peat to increase the calorific power (peat briquettes).
60-80-119 . . . . .	Freeing tar from water.
100-360 . . . . .	Tar distilling (recovering mineral oils).
600-700 . . . . .	Recovery of tar from lignite.
200 . . . . .	Effluent gases in tar recovery.
80-400 . . . . .	Distilling (refining) mineral oils.
80-200 . . . . .	Recovering ceresin from ozokerite, melting and neutralising.
210-230 . . . . .	Recovering naphthalene.
200 . . . . .	Recovering naphthazarine.
180-205 . . . . .	Distilling carbolic acid.
250 . . . . .	Recovery of salicylic acid.
170 . . . . .	Subliming (purifying) salicylic acid by steam.
60-70 . . . . .	Moulding paraffin.
250 . . . . .	Recovering vaseline.
800-1000 . . . . .	Retort temperature in oil recovery.
500-600 . . . . .	Retort temperature in recovering oil gas from tar oil (Peebles).
1000 . . . . .	Retort temperature in recovering coal gas from coal.
60 . . . . .	Recuperating spent purifying materials in gas works.
950-1200 . . . . .	Manufacture of water-gas from coal, air, and steam.
1300 . . . . .	Carbon monoxide from carbon dioxide and glowing carbon.
450 . . . . .	Formation of Mond gas.

### Wood Industry.

60-100 . . . . .	Drying wood, direct.
130 . . . . .	Hot air for drying wood.
100-160 . . . . .	Impregnating wood (also with tar oils).

Temperature  
Degs. C.

150-170 . . . .	Boiling woody fibre for lignin.
105 . . . . .	Boiling straw fibre for cellulose.
160-180 . . . .	Boiling lignin to cellulose.
125-160 . . . .	Converting cellulose into sugar or alcohol.
118 . . . . .	Boiling lignin with calcium sulphite to cellulose.
150-160 . . . .	Boiling esparto grass to cellulose.
60-200 . . . . .	Preparing artificial wood from sawdust, blood, &c.
300-600 . . . .	Distilling wood for methyl alcohol, wood vinegar.
700-850 . . . .	Illuminating gas from wood.
160-270 . . . .	Carbonising wood to pyrophoric charcoal.
270-430 . . . .	Carbonising wood to charcoal.
1200-1500 . . .	Carbonising wood, maximum temperature.
375-800 . . . .	Preparing carbon dioxide from charcoal.
980-1100 . . . .	Preparing carbon monoxide from charcoal.

**The Ceramic Industry.**

600 . . . . .	Porcelain biscuit kiln.
900-1000 . . . .	Baking fritted porcelain.
900-1000 . . . .	Baking porcelain (boric acid mixture).
1350 . . . . .	Glazing kiln temperature for porcelain.
1500 . . . . .	Glazing kiln temperature for hard porcelain.
260 . . . . .	Kilning Tripoli (gypsum, clay, and coke).
1400 . . . . .	Kilning Portland cement.
120-170 . . . .	Kilning gypsum.
500 . . . . .	Kilning gypsum for hydraulic plaster (alabaster gypsum).
600-900-1200 .	Kilning limestone for quicklime.
1100-1400 . . .	Kilning bricks, tiles.
900-1600 . . . .	Kilning earthenware, clay figures.
108-172 . . . .	Effluent gases from brick kilns.
1200-1250 . . .	Glass furnaces.
1400 . . . . .	The Siemens glass furnace.
7650 . . . . .	Combustion chamber in glass furnace.
700-800 . . . .	Annealing oven in glass works.
600-800 . . . .	Cold stirring in glass smelting.
70-300 . . . . .	Annealing baths for hard glass (fat, paraffin, salts, metals).
100-900 . . . .	Preparing cobalt blue.
1300 . . . . .	Kilning cement.
600-800 . . . .	Kilning water-glass.
1500-1800 . . .	Kilning luminous paint.

**Chemicals.**

The following temperatures are employed in preparing the various products specified:—

100-140 . . . .	Ether.
500 . . . . .	Alum, by roasting.
180-200 . . . .	Ammonia, by distilling its compounds from lime.
200-300 . . . .	Ammonia, charring offal.
70 . . . . .	Ammonium carbonate (sublimation).
160-200 . . . .	Ammonium chloride (sal ammoniac) from dung, urine, organic matter.
140 . . . . .	Ammonium chloride, by sublimation.
100-180 . . . .	Ammonium sulphate from gas and tar water.
400-500 . . . .	Antimony oxide by roasting antimony sulphide.
70 . . . . .	Arsenious acid from arsenic and nitric acid.
108 . . . . .	Formic acid from oxalic acid and glycerin.
500 . . . . .	Hydrocyanic acid from cyanogen gas and hydrogen.
330-350 . . . .	Benzoic acid from naphthalene.
600 . . . . .	Lead from lead sulphide by electrolysis.
700-950 . . . .	Lead by roasting lead ores.
700-850 . . . .	Lead antimonate (Naples yellow).

Temperature  
Degs. C.

300 . . . . .	Lead protoxide from lead oxalate.
450 . . . . .	Lead oxide (red lead, minium).
450 . . . . .	Lead chromate from chrome yellow and saltpetre.
334-500 . . . . .	Lead carbonate, English method.
60-90 . . . . .	Lead carbonate, Dutch process.
950 . . . . .	Potassium ferrocyanide by fusing offal.
150-300 . . . . .	Potassium ferrocyanide by charring offal.
100 . . . . .	Potassium ferrocyanide from spent gas lime.
780-900 . . . . .	Bronze for casting bells.
700 . . . . .	Calcium (metallic) by electrolysis.
100 . . . . .	Chloral from alcohol and chlorine.
60-70 . . . . .	Chloroform from alcohol, bleaching powder, and water.
700 . . . . .	Chromium oxide from potassium bi-chromate and boric acid.
400 . . . . .	Chlorine gas from HCl and steam (Deacon).
60 . . . . .	Bleaching powder.
500-600 . . . . .	Potassium cyanide from ferrocyanide.
900 . . . . .	Potassium cyanide from potash, carbon, and ammonia.
1100 . . . . .	Potassium cyanide from sugar refinery waste.
30-40 . . . . .	Vinegar by fermentation.
120-130 . . . . .	Vinegar by distillation.
200-300 . . . . .	Freeing acetates from tarry impurities.
500 . . . . .	Ferrous sulphate as a bye-product in alum manufacture.
1300 . . . . .	Potassium (metallic) by electrolysis.
525-700 . . . . .	Potassium chromate from chrome ironstone.
525 . . . . .	Potassium chromate from chromic oxide.
930-1200 . . . . .	Potassium sulphate from potassium chloride.
700-1200 . . . . .	Potassium carbonate from potassium sulphate.
700 . . . . .	Potash salts by calcining vegetable matter.
525-700 . . . . .	Potassium sulphate from potassium sulphite.
450-500 . . . . .	Copper sulphate from copper sulphide.
230-350 . . . . .	Magnesium sulphate from dolomite.
1300 . . . . .	Sodium (metallic) by electrolysis.
300-400 . . . . .	Sodium peroxide from sodium and air.
930-1200 . . . . .	Sodium sulphate in soda manufacture.
713-1200 . . . . .	Sodium carbonate (soda), Leblanc process.
500-532 . . . . .	Sodium carbonate (soda), Hargreaves' process.
400-500 . . . . .	Sodium nitrite from saltpetre.
300 . . . . .	Sodium stannate from roasted tinstone.
500 . . . . .	Temperature attained in alkali waste, by spontaneous heating.
180 . . . . .	Decomposition of ferrocyanogen compounds in crude soda lye.
60-70 . . . . .	Nitrobenzol by the nitration of benzol.
200-250 . . . . .	Oxalic acid from sawdust and caustic potash.
122 . . . . .	Fusing point of picric acid.
200-210 . . . . .	Pyrogallic acid from gallic acid.
230 . . . . .	Tin phosphide from molten tin.
230-250 . . . . .	Red phosphorus from white phosphorus.
500-600 . . . . .	White phosphorus from metaphosphoric acid and zinc.
950-1000 . . . . .	White phosphorus from calcium phosphate (bones).
200 . . . . .	Mercury bi-chloride (sublimite).
500-600 . . . . .	Sulphocyanide (thiocyanate) compounds from ferrocyanide, potash, and sulphur.
200-400 . . . . .	Oxygen from cuprous chloride.
850 . . . . .	Oxygen from soda, manganese dioxide, and steam.
400-600 . . . . .	Oxygen from manganese dioxide and potassium chlorate.
360-400 . . . . .	Oxygen from potassium chlorate.
500-1000 . . . . .	Oxygen from barium peroxide.
230 . . . . .	Nitric acid from chlorine residues and saltpetre.
130-300 . . . . .	Nitric acid from saltpetre and sulphuric acid.
86-123 . . . . .	Nitric acid (distillation temperature).
110-112 . . . . .	Flowers of sulphur.
130 . . . . .	Sulphur by liquation.
140-150 . . . . .	Sulphur by steam.
448 . . . . .	Sulphur (sublimation temperature).

Temperature  
Degr. C.

450-850 . . . .	Hydrochloric acid from soda cake ovens.
400 . . . . .	Sulphurous acid from sulphuric acid and sulphur.
40-80 . . . . .	Sulphuric acid in the leaden chamber.
135-338 . . . .	Sulphuric acid (chamber acid), concentration temperature.
60-130 . . . . .	Temperature in the Glover tower.
600-700 . . . .	Fuming sulphuric acid from sodium bisulphate.
130 . . . . .	Sulphur chloride from chlorine and sulphur.
450 . . . . .	Iron chloride from iron filings and sulphur.
450-520 . . . .	Carbon disulphide from sulphur vapour and glowing iron.
114-115 . . . .	Mercury sulphide (vermilion) from mercury and sulphur.
400-600 . . . .	Permanganates from manganese dioxide and potassium.
700-1200 . . . .	Ultramarine from sulphur, clay, soda, charcoal.
800 . . . . .	Hydrogen gas from steam and glowing metals.
700-800 . . . .	Hydrogen peroxide from baryta and oxygen.
100 . . . . .	Tartaric acid.
140-170 . . . .	Tartaric acid from crude tartar, by steam.
500 . . . . .	Zinc oxide by the combustion of zinc.
520-700 . . . .	Tin sulphide from tin amalgam, sulphur, and sal ammoniac.

**Preparation of Organic Dyestuffs 100°-290° :—**

160-180 . . . .	Aniline blue.
240 . . . . .	Aniline brown.
190-200 . . . .	Aniline red.
270-290 . . . .	Alizarine.
160-200 . . . .	Auramine.
120-130 . . . .	Aurine.
190-200 . . . .	Coeruleine.
250 . . . . .	Diphenylamine.
180-205 . . . .	Fluoresceine.
190-200 . . . .	Galleine.
110 . . . . .	Murexide.
130-140 . . . .	Naphthalene red (Magdala red).
100 . . . . .	Orchil.
170 . . . . .	Phthalic acid.
150 . . . . .	Purpuric acid (Madder purple).
130-140 . . . .	Quinoline.
240-270 . . . .	Resorcine.

**Heating-Bath Temperatures.**(See "*Laboratories*" in *Text*)**Soap and Oil Industries.**

60-90 . . . . .	Warming up the oilseed (meal).
90 . . . . .	Freeing vegetable oils from albumin.
240 . . . . .	Bleaching oils (palm oil).
100-150 . . . .	Distilling ethereal oils.
100 . . . . .	Distilling rose oil.
90-280 . . . . .	Recovery of lubricating oils.
100 . . . . .	Purifying train oil.
120-160 . . . .	Converting liquid fats (oils) into a solid form (linoxin).
150-160 . . . .	Boiling soap by steam.
80 . . . . .	Soap-making by the wet process.
182 . . . . .	Lime saponification.
200-315 . . . .	Converting fats into fatty acids and glycerin in the autoclave.
115-177 . . . .	The same operation with sulphuric acid.
170 . . . . .	Preparation of stearic acid from fat and lime.
40-70 . . . . .	Warm pressing oleic acid.
250-350 . . . .	Distilling fatty acids.

Temperature  
Degs. C.

320 . . . . .	Preparation of palmitic acid from oleic acid and potash.
310 . . . . .	Recovering glycerin.
200 . . . . .	Distilling glycerin.
45-70. . . . .	Temperature of the moulds for stearin candles (45°-50°), paraffin candles (60°-70°).

### Resin, Wax, Lacquer, and Rubber Industries.

270-300 . . . . .	Recovery of resin oil in resin distillation.
50-280 . . . . .	Melting resin for varnish or sealing wax.
200-400 . . . . .	Boiling linseed oil for varnish.
50-75. . . . .	Temperature in the lacquering stove.
138-300 . . . . .	Spontaneous heating in varnish filters.
230-310 . . . . .	Heating linseed oil for printers' ink.
70-86. . . . .	Running (purifying) animal and vegetable waxes.
112-150 . . . . .	Vulcanising caoutchouc and gutta-percha with sulphur.
15-25. . . . .	Cold vulcanising process for caoutchouc.
160 . . . . .	Hardening caoutchouc to ebonite.
15-20. . . . .	Vulcanising caoutchouc with carbon disulphide.
25 . . . . .	Drying vulcanised caoutchouc.
130-140 . . . . .	Blowing rape oil with hot air in making imitation rubber.
160 . . . . .	Boiling rape oil with sulphur for same purpose.

### Tanning, Glue Manufacture.

26-50. . . . .	Temperature of the sweating tank.
50 . . . . .	Warming the skins for oiling.
35 . . . . .	Temperature of the dung vat (often much higher).
100 . . . . .	Temperature of the oiled skins (tawing, shamoying); often higher.
50 . . . . .	Varnishing temperature for leather.
100-112 . . . . .	Boiling glue stock.
150 . . . . .	Preparation of steam glue.
20 . . . . .	Drying glue.
80-85. . . . .	Converting dry glue into liquid glue.
30 . . . . .	Preparation of adhesive glue.
140 . . . . .	Temperature for softening hard cement.

### Match Industry.

950-1000 . . . . .	Calcining bones for phosphorus.
230-250 . . . . .	Converting white phosphorus into red variety.
260-290 . . . . .	Converting red phosphorus into white variety.
213 . . . . .	Preparation of pyrophosphoric acid from orthophosphoric acid.
115 . . . . .	Melting sulphur for dipping match-sticks.
50 . . . . .	Softening the match paste.
30 . . . . .	Drying phosphorus matches.

### Sugar Industry.

50-66. . . . .	Temperature of diffusion pans.
85-100 . . . . .	Temperature of separating pans.
65-107 . . . . .	Temperature of evaporators.
50-88. . . . .	Temperature of the "masse cuite."
60-90. . . . .	Boiling the juice to granulate.
100-120 . . . . .	Temperature in the beet residue presses.
75-115 . . . . .	Temperature of sugar-candy juice.
140-220 . . . . .	Converting sugar into caramel, and sugar colouring.
600-900 . . . . .	Kilning the lime.
150-800 . . . . .	Slaking the lime.

**Fibres and Textiles.**

Temperature Degs. C.	
100-150 . . . .	Carbonising wool, &c.
90-95 . . . .	Scouring silk.
100 . . . .	Boiling silk.
50 . . . .	Dyeing temperature for fibres.
85-200 . . . .	Gassing textiles and yarns.

**Fermentation Industries: Starch-making.**

10-15 . . . .	Malting-floor temperature.
30-60 . . . .	Malt kiln.
100 . . . .	Roasting malt.
15-25 . . . .	Spontaneous heating of germinating malt.
30-75 . . . .	Mashing temperature.
100 . . . .	Boiling wort in the copper.
150 . . . .	Sterilising the yeast-culture apparatus.
25-28 . . . .	Fermentation temperature (cultivation temperature of yeast = 25°).
5-30 . . . .	Fermentation of wine.
24 . . . .	Fermentation in bottle.
38-45 . . . .	Lactic fermentation.
50-70 . . . .	Distillery mash temperature.
125-145 . . . .	Steaming potatoes and maize for distillery work.
40 . . . .	Spontaneous heating of potato pulp in the heap.
60-80 . . . .	Temperature of drying rooms for levigated starch; gelatinising starch.
60-75 . . . .	Converting starch into maltose or dextrose with diastase.
80-200 . . . .	Converting starch into dextrose, dextrin (200°-400°) with acids, by steaming under pressure.
125-160 . . . .	Converting wood (cellulose) into sugar (spirit).
124-145 . . . .	Converting cellulose into sugar by acids and steam pressure.
88-112 . . . .	Conversion temperature in spirit stills.

**Preserving Foodstuffs, &c.**

65 . . . .	Pasteurising.
105-110 . . . .	Sterilising.
60-150 . . . .	Roasting cocoa nibs.
200-250 . . . .	Roasting coffee beans.
40 . . . .	Drying of fruits for preserving.
140-150 . . . .	Final drying of fruits for preserving.
100 . . . .	Desiccating fruit.
200-250 . . . .	Bake ovens for bread.
52 . . . .	Preliminary drying egg albumin.
100-110 . . . .	Final drying egg albumin.
170 . . . .	Drying prepared foods (from blood, albumin, &c.).

**Divers Working Temperatures.**

95-100 . . . .	Low pressure hot water heating (up to 130°).	
130-140 . . . .	Medium pressure hot water heating.	
140-150 . . . .	High pressure hot water heating (up to 200°).	
102-106 . . . .	Low pressure steam heating.	
106-126 . . . .	High pressure steam heating.	
Up to 500 . . . .	Temperature of hot air for heating purposes (at the furnace).	
300 . . . .	Hot bottles with fused sodium acetate.	
Up to 2000 . . . .	Coal dust firing.	
800 . . . .	Gas temperature at entrance of furnace.	} Generator gas firing.
600 . . . .	Heated air.	
1500-2000 . . . .	Gases of combustion in the chambers.	
500-550 . . . .	Gases of combustion on entering flue.	
1200 . . . .	Furnace gases from boiler firebox.	
200-300 . . . .	Furnace gases on entering chimney-stack.	

Temperature Degs. C.	
600-1000 . . .	Refuse destructors (combustion).
300-400 . . .	Refuse destructors (gasification).
1200-2000 . . .	Refuse destructors (fusion).
107-194 . . .	Heating compressed air for motive power.
1300-1400 . . .	Temperature in burning houses.
80 . . . . .	Hot running machinery (may extend to 500°).
50-160 . . . .	Disinfecting articles of use by steam.
2000-5000 . . .	Temperature of electric arc lamp flame (see <i>Lighting</i> ).
525-1500 . . .	Incandescence temperatures (see text).

### TABLE III.—EXPLANATORY OF SOME OF THE CHIEF WORKING PROCESSES AND THEIR RISKS

**Alcoholising.**—Reducing substances to an extreme state of fine division, by trituration or solution, and evaporating the solution to dryness on some porous body like sponge or textile fabrics. Substances thus treated (phosphorus, spongy platinum, powdered charcoal, iron sulphide) have a great affinity for oxygen and consequent tendency to spontaneous ignition.

**Amalgamating** (see text).

**Annealing Metals.**—Producing certain colours on metal by plunging the glowing metal into a bath of metal (220°-290° C.) or oil (316° C.). For the dangers of the process, see *Hardening Metals* and *Laboratory Baths*.

**Animalising Fibres.**—Treating vegetable fibres with albuminous substances (casein, albumin) to facilitate the absorption of dyestuffs. No danger.

**Blackening Metal.**—To produce a dull black surface on metal objects they are thinly coated with free-burning oil, fat, wax, paraffin, or petroleum residue, &c., then shaken and heated over a charcoal fire, a thin stratum of carbon being deposited on the metal by the carbonisation or combustion of the coating. May be dangerous from the formation of combustible or explosive gases.

**Briquetting.**—Converting pulverulent and waste materials into a form convenient for handling and use.

Is chiefly applied to the production of coal briquettes (*q.v.*), an operation attended by high fire and explosion risks.

Ores are briquetted by mixing the powdered material with naphthalene, resin, or paraffin, and then exposing to a heat of 400°-500° C., which expels and consumes the gaseous cementing medium. Risk of fire and explosion.

**Burning** (see also *Gases*).—1. Ceramic articles (lime, gypsum, cement, porcelain, clay) in strongly heated kilns. The temperatures are 125° C. (gypsum) to 1500° C. (porcelain).

2. Ores: heating at high temperatures away from the air (in contradistinction to roasting in air).

3. Wooden articles: pressing the wood between strongly heated metal moulds. Not without danger, owing to the formation of pyrophoric carbon and inflammable gases. (See *Wood*.)

4. Alcoholic masses: distillation for recovering alcohol. Temperature 112° C.; danger of ignition and explosion of the hot vapour of alcohol.

**Calcination.**—Heating to redness ores, chemicals (soda, potash, and salts), to expel volatile constituents (water and carbon dioxide), destroy organic matter, and loosen the mass. Very high temperatures.

**Carbonising** (see text, *Fibrous Materials*).—Peat is carbonised to peat charcoal, first at 250° C., and then at 300° C. in closed ovens. Hartmann process, in the open air, at 220° C. The resulting gases are highly inflammable and explosive.

**Carburetting** (see text, *Gases*).

**Case-Hardening Metal.**—Heating cast iron to redness in charcoal powder, or dipping the glowing object in molten pig iron, fat, or fat and ferro-cyanide, to convert the exterior into steel. Attended with the risks incidental to fats and glowing metals.

**Charring.**—Heating organic substances, out of contact with air, till the con-

stituents volatile at dull red heat have been eliminated (see *Wood Charcoal*). Inflammable and explosive gases are formed.

**Coking.**—The charring of coal and coal-dust in coke ovens for the recovery of coke, tar products, and mineral oils. The risks are great, owing to the formation of numerous inflammable and explosive vapours.

**Coppering Textiles.**—Imparting a metallic lustre to textile fabrics by impregnation with dissolved salts of copper or lead, and then treating them with steam charged with sulphuretted hydrogen. The latter being dilute, there is no danger.

**Correcting.**—Altering the condition of substances that are too hard or too soft by certain additions, *e.g.* softening clay by glycerin, and wax by oil of turpentine. Not risky unless the materials are dangerous.

**Creosoting (Bethellising).**—Impregnating wood with creosote. The wood acquires a greater tendency to spread flame.

**Cupellation.**—Smelting gold and silver ores, alloys, or lead in cupel furnaces, the other metals being oxidised and eventually fused, leaving the gold and silver unaltered.

**Cyanising.**—Impregnating wood, &c., with mercury bichloride. No danger.

**Decarburising (Puddling, Bessemerising) Iron.**—By blowing air under strong pressure into molten pig iron the latter is freed from impurities and a portion of its carbon, to convert it into wrought iron. High temperatures, the formation of combustible carbon monoxide gas, and the glowing slag introduce danger into the process.

**Denaturing.**—Rendering a substance unfit for human consumption by additions that do not affect its technical utility. Thus, common salt is denatured with ferric oxide, wormwood powder, charcoal, Glauber salt, soap, petroleum, or carbolic acid; spirits with pyridin, wood spirit, oil of turpentine, or animal oil. The only really dangerous adjunct is wood spirit (see *Alcohol*).

**Denitration** (see *Nitration*).—Eliminating the nitro group from a nitrated substance by treatment with sulphur compounds (potassium sulphide), thus removing the tendency to take fire and explode (see *Artificial Silk*). The nitrous fumes (sulphuric and nitrosulphuric acid) from the manufacture of sulphuric acid are denitrated by means of steam. Operation is free from objection; nevertheless, see *Nitric Oxide*, which is also formed.

**Dephlegmation.**—Eliminating water vapour from the vapours of other liquids, especially alcohol, in carefully cooled apparatus (dephlegmators). Also applies to the separation of various gases and vapours that condense at different temperatures, the least volatile liquefying first, leaving the lighter portions to pass on through the apparatus and be condensed later. The risks are great when inflammable and explosive gases and vapours are in question.

**Desulphurising.**—Expelling sulphur from metallic sulphides, pyrites, glance, blende, and other sulphuritic substances, by roasting in air. High combustion temperature.

**Dry Distillation.**—Imperfect combustion of coal and similar substances in semi-closed vessels. Inflammable and explosive gases are formed (see *Stove Explosions*).

**Encausticising.**—Dipping gypsum and similar articles in fat, paraffin, or soap, at 60°–90° C., to impart an appearance of ivory. Heating is sometimes dispensed with by the employment of solvents for the fat, &c.; but this renders the operation dangerous, owing to the explosive vapours furnished by the solvents in question (petroleum ether, benzol, or ether).

**Evaporating.**—Expelling liquid solvents by heat. If all the volatile portions of the solvent are driven off, the operation is termed “evaporating to dryness.” When dealing with solvents, like ether or benzol, which give off inflammable and explosive vapours, the evaporation should be effected with heating liquids (baths; see *Laboratories*), all direct flame being avoided. Where large quantities of liquid are in question (sugar refineries), the evaporation is conducted in vacuum pans.

**Fermenting.**—Piling moistened organic substances in heaps to enable them to undergo a process of fermentation accompanied by spontaneous heating (dyewoods, tobacco, hay, leather). Under certain circumstances, the heating may extend to the point of spontaneous ignition.

**Fritting (Sintering).**—In many instances, loose substances when heated soften and cohere, without actually melting. Moderately high temperature only is required.

**Fulminating.**—Allowing substances (mostly fulminates, *q.v.*) to detonate or explode.

**Gassing.**—Passing yarns, silk, or textiles through a small gas flame, or over glowing metal plates, to burn away the finest fibres (down). Under certain circumstances the fire risk may be very considerable; a large amount of carbon monoxide gas is produced; sometimes the necessary gas is produced on the premises, in air-gas apparatus (*q.v.*). The work should be done in the forenoon so that the goods can be examined later for the presence of any glimmer or sparks in the material; or the whole parcel can be looked through in the evening.

**Glazing.**—Same as lacquering, with transparent lacquer or varnish, *e.g.*, leather.

**Grading Ores.**—Mixing poor and rich ores together so as to obtain the most favourable ratio of slag to metal. No danger.

**Granulating.**—Disintegrating molten substances (phosphorus, metals) by dropping or pouring into moving water. With refractory metals the water may be decomposed and explosive oxyhydrogen gas formed (danger of explosion). Phosphorus easily ignites when shaken up, in the granulated condition, with water.

**Kilning** (see *Roasting*).—Drying on a large scale, with simultaneous production of chemical changes in vegetable products like barley, wheat, fruit, chicory, and carrots. Lower temperatures than in roasting (*q.v.*). Possible formation of pyrophoric carbon. Owing to the risk of sparking, the grinding of kiln-dried products by machinery is dangerous.

**Liquation** (in Metal Refining).—Separating the more fusible metals from two or more ores, &c., by smelting on a sloping hearth, down which the molten portions flow, leaving the more refractory metals behind (process adopted with bismuth, antimony, lead, and tin). The sole danger is from the high temperature.

**Lacquering (Varnishing).**—Coating objects with lacquer or varnish, and drying at 50°–75° C. See *Varnish* for the dangers. When the articles are *dipped* the operation is termed “varnishing.”

**Loading Textiles.**—Increasing the weight of fibres with extraneous substances. For dangers see *Silk*.

**Luting.**—Cementing with oil, varnish, or resinous cements. No danger.

**Macerating.**—A harmless method of extracting substances with a liquid, without the use of heat.

**Mercerising** (after Mercer).—Imparting gloss to cotton fibres by treating the tightly stretched fibres with caustic soda, followed by washing and drying. Harmless.

**Metallising.**—Coating articles by dipping in molten metal. Also impregnating fabrics and fibres with soluble metallic salts. Latter process unobjectionable; the former may prove risky through the high metal temperature.

**Millerrainising.**—Impregnating textiles, especially silk, with aluminium acetate and coating with molten fat. The latter treatment is calculated to render the textiles liable to spontaneous ignition.

**Mordanting.**—Impregnating textiles with decoctions of tannin, &c. Innocuous itself, though a possibility of spontaneous ignition is afforded when ferrous compounds are used at the same time (see *Silk*).

**Neutralising** (see *Salts, Acids, Oxides*).—Depriving an acid of its acid properties by means of an oxide (base), or *vice versa*. In both cases salts are formed and heat disengaged. Unless the operation is conducted in dilute solutions, considerable heat is generated, and the reaction may assume an explosive character.

**Nitrating** (see text).

**Oxidising.**—Combining an element, or compound, with oxygen. Oxidation may be considered as chemically equivalent to combustion (*q.v.*). The reaction may proceed very gradually, with or without flame, or with explosive rapidity.

**Paraffining.**—Protecting objects from damp or putrefaction by impregnation with paraffin solutions. The articles are rendered more inflammable and combustible. As the solvents (petroleum ether, benzol, or carbon disulphide) are very dangerous, and give off explosive vapours on evaporation, the process is attended with great risk.

**Parkes Desilverising Process.**—Adding zinc to molten silver-lead (420°–430° C.), to recover the silver. Apart from the high temperature there is no danger.

**Pattinson Desilverising Process.**—Allowing the low-grade silver-lead to crystallise out from the molten metal (334° C.) and pouring off the portion richer in silver. No danger, except from the high temperature.

**Pickling.**—Chemically cleaning the surface of metal objects by dipping in nitric or sulphuric acid. Paper, straw, shavings, wood wool, &c., must be kept out of the way (see *Carbon Explosions*).

**Protecting Iron.**—Blowing superheated steam (6 atmos. pressure) into strongly heated iron pipes to form an anti-corrosive lining of iron protoperoxide. Explosive oxyhydrogen gas may be formed.

**Quenching** (see *Annealing Metals*).—Interrupting a process of combustion, or heating to redness, by a sudden cooling, effected usually by water or oil. Glowing metals are also quenched to remove an external layer formed during heating. The quenching of large quantities of coke, metal, or slag, with water, may produce oxyhydrogen gas (explosion).

**Reducing.**—The antithesis of oxidation; depriving a substance of oxygen. Here also the reaction may proceed at the ordinary temperature, *e.g.* under the influence of nascent hydrogen; or at a high temperature, *e.g.* by calcination in presence of carbon.

**Refining.**—Purifying and improving substances, especially in the sugar and mineral oil industries. In the former case no danger, in the latter much (*q.v.*).

**Refining Gold and Silver.**—The elimination of copper from gold and silver by treatment with sulphuric acid and heating, sulphur dioxide being formed. No great danger.

**Resinification or Gumming.**—When exposed to the air, ethereal oils and resins absorb oxygen (oxidise), and gradually become more and more solid, *i.e.* they resinify. This alteration renders them more dangerous, since they become carriers of oxygen and also produce ozone.

**Retting.**—The steeping of flax and hemp, to liberate the fibres. According to R. Baur, the temperature is below 100° C.

**Revivifying Silk.**—Boiling the dyed silk with soap and stannous chloride. Safe.

**Roasting** (see *Kilning*).—Kilning at high temperature (chicory, coffee at 200°–250° C., cocoa at 150° C.). Dextrin is roasted with superheated steam at 300°–400° C. The roasting of ores (with access of air, see *Burning*) is performed at very high temperatures, 700°–950° C.; but as the plant is fireproof there is little danger.

**Roughing or Raising.**—A harmless removal of loose woollen fibre from cloth.<sup>1</sup> In small rooms and with defective ventilation, clouds of wool dust are produced, and these will explode in contact with flame, take fire when deposited on hot pipes, or ignite spontaneously when greased by lamp oil or lubricating oil. The rooms should be well ventilated, and all dust removed from hot pipes.

**Saponification.**—Decomposing fats into glycerin and fatty acids (see *Soap-making*).

**Solidifying.**—Converting one substance into the solid form by means of another. Inflammable liquids (alcohol, petroleum) are absorbed in large quantities by fatty acids, paraffin, and soap. For the dangers, see *Petroleum, Alcohol*.

**Sublimation.**—Vapourising a solid substance by heat, and then reconvert it direct into the solid form by cooling, without the liquid stage intervening at all. When the vapours condense into the liquid form, the operation is termed distillation (see *Wood Charcoal*).

Sublimation mostly occurs at merely moderate temperatures: sal ammoniac, 140° C.; iodine, 110° C.; camphor, 20° C.; ammonium carbonate, 70° C.; oxalic acid, 150° C.; phthalic acid, 300° C.; sulphur, 448° C. Mostly harmless (see *Dust Explosions*). The heat of the sun's rays is sufficient to sublime camphor and naphthalene.

**Sulphating.**—Converting chlorides (in particular) into sulphates, *e.g.* in soda manufacture, where temperatures up to 1200° C. are required. There is, however, no great danger.

**Tarring.**—Coating walls, roofs, woodwork, bricks, millboard, &c., with tar, previously heated to 200° C. Highly dangerous on account of the inflammable vapours liberated.

**Tempering (Decarbonising).**—Metals containing carbon (cast iron) are freed from a portion of same by heating them to redness with oxidising agents, or adjuncts poor in carbon. Very high temperatures required.

**Varnishing** (see *Lacquer*ing).

**Vulcanising** (making Caoutchouc elastic for all temperatures up to 100° C.).—Mixing and combining sulphur with caoutchouc and gutta percha, in the former case by means of molten sulphur at 120°–150° C. Caoutchouc is vulcanised when 15 per cent. of sulphur has been absorbed; and ebonised when the amount reaches

<sup>1</sup> *Translator's Note.*—The primary object of this operation, as the name implies, is to raise the fibres so as to form a pile on the surface of the goods.

30-60 per cent. Gutta percha is vulcanised with sulphur or hyposulphites and at 140°-160° C.

In the cold process of vulcanising, the caoutchouc is dipped into a solution of 6 per cent. of sulphur chloride and carbon disulphide. The use of the latter renders this process highly dangerous. Hot vulcanising is effected under high pressure, and is therefore attended with no slight risk.

**TABLE IV.—MEANING OF VARIOUS CHEMICAL TERMS NOT SPECIALLY EXPLAINED IN THE TEXT**

Acetates . . . . .	Acetic acid compounds.
Albumins . . . . .	Albuminous bodies.
Alcoholates . . . . .	Compounds of alcohol with salts, <i>e.g.</i> calcium chloride.
Alkaline . . . . .	Basic, caustic; antithesis of acid.
Alkaline earths . . . . .	Calcium, barium, strontium.
Alkalis (Alkali metals) . . . . .	Potassium, sodium, lithium, caesium, rubidium.
Alkaloids . . . . .	Nitrogenous alkaline compounds (those of plants especially), caffeine.
Aluminates . . . . .	Compounds of alumina with potassium or sodium.
Anhydrides . . . . .	Compounds free from water (see <i>Hydrates</i> ).
Arsenates . . . . .	Compounds of arsenic acid.
Arsenites . . . . .	Compounds of arsenious acid.
Aurates . . . . .	Compounds of auric acid.
Azides . . . . .	Compounds of metals with nitrogen (nitrides).
Basic . . . . .	See <i>Alkaline</i> .
Benzoates . . . . .	Benzoic acid compounds.
Blendes . . . . .	Compounds (ores) of zinc and sulphur.
Borates . . . . .	Boric acid compounds.
Bromates . . . . .	Bromic acid compounds.
Bromides . . . . .	Compounds of bromine with metals (potassium bromide).
Butyrates . . . . .	Butyric acid compounds.
Camphenes . . . . .	Ethereal oils destitute of oxygen (oil of turpentine, lemon oil).
Carbohydrates . . . . .	Consist of carbon, hydrogen, and oxygen. They include: sugars of all kinds, flour, starch, gum, dextrin, cellulose, fats, oils, and all substances bearing names terminating in -ose.
Carbonatation . . . . .	Conversion of common salt into sodium bicarbonate, and finally into soda.
Carbonates . . . . .	Carbonic acid compounds.
Carburets . . . . .	Carbides.
Chlorides . . . . .	Compounds of chlorine with metals (iron chloride).
Chlorites . . . . .	Chlorous acid compounds.
Chromites . . . . .	Compounds of chromic oxide with metals.
Citrates . . . . .	Citric acid compounds.
Cremonites . . . . .	Detonating preparations, partly composed of picrates.
Cyanates . . . . .	Cyanic acid compounds.
Cyanides . . . . .	Compounds of cyanogen with elements or metals.
Earthy metals . . . . .	Boron, aluminium, gallium, indium, thallium.
Elements . . . . .	Substances that cannot be decomposed by any chemical means.
Fluorides . . . . .	Compounds of fluorine with metals (calcium fluoride).
Formates . . . . .	Formic acid compounds.
Glance . . . . .	Compounds (ores) of sulphur with copper, lead, or bismuth.
Glycerates . . . . .	Solutions of alkalis or lead oxide in glycerin.
Glycolate . . . . .	Compounds of glycolic or oxyacetic acid.
Halogens . . . . .	The elements chlorine, bromine, iodine, fluorine.
Hydrate . . . . .	Compound of a salt, oxide, or acid with water.

Hydride . . . . .	Compound of a metal with hydrogen.
Hydrocarbons . . . . .	All compounds of carbon and hydrogen (benzol, naphthalene).
Hyper- (Per-) . . . . .	Super-, (super-, hyper-, or peroxide).
Hypo- . . . . .	Sub-, under- (hypochlorous acid).
Iodide . . . . .	Compound of iodine with a metal.
Lactate . . . . .	Lactic acid compound.
Light metals . . . . .	Metals specifically lighter than water (potassium, sodium, &c.)
Malate . . . . .	Malic acid compound.
Malonate . . . . .	Malonic acid compound.
Manganate . . . . .	Manganic acid compound.
Manganite . . . . .	Compound of manganese dioxide.
Metalloid . . . . .	See <i>Non-metals</i> .
Molybdate . . . . .	Molybdic acid compound.
Non-metals . . . . .	Elements devoid of metallic properties (carbon, phosphorus).
Oleate . . . . .	Oleic acid compound.
Oxalate . . . . .	Oxalic acid compound.
Palmitate . . . . .	Palmitic acid compound.
Paralactate . . . . .	Paralactic acid compound.
Peptone . . . . .	Uncoagulable by gastric or pancreatic juice, and therefore directly digestible albuminoid.
Per-compound . . . . .	Compound of a peracid (permanganate).
Permanganate . . . . .	Permanganic acid compound.
Phosphate . . . . .	Phosphoric acid compound.
Phosphite . . . . .	Phosphorous acid compound.
Phthalate . . . . .	Phthalic acid compound.
Propionate . . . . .	Propionic acid compound.
Proteins . . . . .	Resembling albumin.
Ptomaines . . . . .	Alkaloids, chiefly produced during putrefaction.
Pyrophores . . . . .	Substances glowing and igniting spontaneously.
Resinate . . . . .	Resinic acid compound.
Saccharate . . . . .	Compound of sugar with lead, calcium, &c.
Selenate . . . . .	Selenic acid compound.
Selenite . . . . .	Selenious acid compound.
Silicate . . . . .	Silicic acid compound.
Silicide . . . . .	Compound of silicon with metals (iron silicide).
Slag . . . . .	Compound of silica with metals, lime, and clay.
Soap . . . . .	Compound of fatty acids with alkalis.
Stannate . . . . .	Stannic acid compound.
Stearate . . . . .	Stearic acid compound.
Stibine . . . . .	Compound of antimony with organic substances.
Styphnate . . . . .	Styphnic acid compound.
Succinate . . . . .	Succinic acid compound.
Sulphate . . . . .	Sulphuric acid compound.
Sulphide . . . . .	Compound of sulphur with a metal.
Sulpho-compound . . . . .	See <i>Thio-compound</i> .
Tartrate . . . . .	Tartaric acid compound.
Telluride . . . . .	Compound of tellurium with a metal.
Terpenes . . . . .	Volatile oils of coniferous resins.
Thio-compound . . . . .	Sulpho-compound; compound with a sulpho group.
Titanate . . . . .	Titanic acid compound.
Toxines . . . . .	See <i>Ptomaines</i> .
Uranate . . . . .	Uranic acid compound.
Urate . . . . .	Uric acid compound.
Urethanes . . . . .	Compounds of carbamic acid with ethers.

TABLE V.—BOILING-POINTS OF LIQUIDS BELOW 50° C.

Degs. C.	
20·8 . .	Aldehyde, acetaldehyde, ethyl aldehyde.
36·0 . .	Ammonium cyanide.
39·0 . .	Amylene, a. (propylethylene).

Degs. C.	
36.0 . .	Amylene, $\beta$ . (methylethylethylene).
31.0 . .	Amylene, $\gamma$ .
38-42. . .	Anaesthetics (mixtures of ether, petroleum ether, chloroform, &c.)
37.0 . .	Azoimide (hydronitrous acid).
18.0 . .	Boron chloride.
16.0 . .	Bromoethylene (vinyl bromide).
48.0 . .	Bromopropylene, $\beta$ .
1.0 . .	Butane (diethyl).
36.0 . .	Cacodyl chloride (dimethylarsenic chloride).
46.0 . .	Carbon disulphide.
8.0 . .	Carbon oxychloride (carbonyl chloride, phosgene gas).
15.5 . .	Chlorocyanogen.
35.0 . .	Chloropropylene, $\alpha$ .
23.0 . .	Chloropropylene, $\beta$ .
46.0 . .	Chloropropylene, $\gamma$ . (allylchloride).
28.0 . .	Crotonylene (dimethylacetylene).
41.0 . .	Cyclopentanes.
37.0 . .	Dichlorethylene.
7.2 . .	Dimethylamime.
40.0 . .	Dimethylpropine.
25.0 . .	Dimethylphosphine.
20-30. . .	Divinyl.
39.0 . .	Divinyl ether.
35.5 . .	Ether (ethyl ether, &c.)
18.0 . .	Ethylacetylene.
37.0 . .	Ethylallyl.
18.7 . .	Ethylamime.
38.5 . .	Ethyl bromide (bromoethyl).
12.5 . .	Ethyl chloride (chloroethyl).
13.5 . .	Ethylene oxide (ethylene ether, glycol ether).
16.4 . .	Ethyl nitrite (nitrous ether).
25.0 . .	Ethylphosphine.
36.0 . .	Ethyl sulphhydrate (mercaptan).
32.3 . .	Formic methyl ether (methyl formate).
31.6 . .	Furfurane.
20.0 . .	Hypochlorous anhydride.
10.0 . .	Hypochloric anhydride (chlorine tetroxide).
26.5 . .	Hydrocyanic acid (formonitrile).
21.3 . .	Isoamylenes, $\alpha$ . (isopropylethylene).
37.0 . .	Isoamylenes, $\beta$ . (trimethylethylene).
30.0 . .	Isopentane (dimethylpropane, dimethylethylmethane amyl hydride).
34.0 . .	Isoprene.
28.0 . .	Isopropylacetylene.
32.0 . .	Isopropylamine.
37.0 . .	Isopropyl chloride.
36.0 . .	Isopropyl alcohol.
45.0 . .	Isopropyl nitrite (nitrous isopropyl ether).
41.0 . .	Isopropylphosphine.
11.0 . .	Methylethylether (ethylmethyl ether).
42.0 . .	Methylal (methylenedimethyl ether).
4.5 . .	Methyl bromide (bromomethane, bromomethyl).
41.5 . .	Methylene chloride.
44.0 . .	Methyl iodide (iodomethyl, iodomethane).
37.0 . .	Methylpropyl ether.
21.0 . .	Methyl sulphhydrate (methyl mercaptan).
37.5 . .	Methyl sulphide.
43.0 . .	Nickel carbon monoxide.
50.0 . .	Nitric anhydride (nitrogen pentoxide).
26.0 . .	Nitrogen tetroxide.
22.5 . .	Nitrosyl bromide.
5.0 . .	Nitryl chloride.
45.0 . .	Pentamethenylene.
50.0 . .	Pentamethylene.

Degs. C.	
37.0 . . .	Pentane (normal).
9.5 . . .	Pentane (tetramethylmethane).
40-70. . .	Petroleum ether (petroleum naphtha).
42.0 . . .	Piperylene.
48.0 . . .	Propylacetylene.
50.0 . . .	Propyl aldehyde (propionaldehyde).
49.0 . . .	Propylamine.
46.5 . . .	Propylchloride.
35.0 . . .	Propylene oxide, $\alpha$ .
50.0 . . .	Propylene oxide, $\beta$ . (trimethylene oxide).
1.0 . . .	Pseudobutylene.
35.0 . . .	Silicon chloroform.
30.0 . . .	Silicon methyl (-tetramethy, silicopentane).
46.2 . . .	Sulphuric anhydride (sulphur trioxide).
43.0 . . .	Trimethylethylmethane (hexane).
3.8 . . .	Trimethylamine.
40.0 . . .	Trimethylphosphine.
20.0 . . .	Turpentine oil distillate (first runnings).
35.5 . . .	Vinylethyl ether.
24.0 . . .	Xanthogenic acid.
46.0 . . .	Zinc methyl.

TABLE VI.—FUSING AND BOILING POINTS

*(Mostly Approximate).*

## 1. Elements.

	F.-p. Degs. C.	B.-p. Degs. C.		F.-p. Degs. C.	B.-p. Degs. C.
Caesium . . . . .	26.0	270	Aluminium . . . . .	660	...
Gallium . . . . .	30.0	...	Magnesium . . . . .	700-800	...
Rubidium . . . . .	38.5	...	Calcium . . . . .	760	...
Phosphorus (white) . . . . .	44.4	278	Germanium . . . . .	900	...
Potassium . . . . .	62.5	667	Beryllium . . . . .	950	...
Sodium . . . . .	97.0	742	Silver . . . . .	960	} white heat
Iodine . . . . .	114.0	184	Gold . . . . .	1060	
Sulphur . . . . .	114.5	448	Copper . . . . .	1080	...
Indium . . . . .	176	} white heat pale red	Nickel . . . . .	1500	...
Lithium . . . . .	180		Uranium . . . . .	1500	...
Selenium . . . . .	217		Tungsten . . . . .	1700	...
Tin . . . . .	233		Palladium . . . . .	1700	...
Bismuth . . . . .	268	1500	Platinum . . . . .	1760	...
Thallium . . . . .	290	1700	Cobalt . . . . .	1700-1800	...
Cadmium . . . . .	320	} white heat	Iron, pure . . . . .	1800	...
Lead . . . . .	334		(a) Cast pig iron . . . . .	1050-1300	...
Zinc . . . . .	412	778	(b) Steel . . . . .	1300-1800	...
Antimony . . . . .	430	1600	(c) Wrought iron . . . . .	1800-2200	...
Arsenic (under pressure) . . . . .	450	950	Manganese . . . . .	1900	...
Tellurium . . . . .	455	1500	Chromium . . . . .	2100	...
Strontium . . . . .	525	...	Iridium . . . . .	2400	...
			Silicon . . . . .	2800	...
			Ruthenium . . . . .	...	...
			Osmium . . . . .	...	...

TABLE VI.—FUSING AND BOILING POINTS (*continued*).

## 2. Alloys, Metallic Mixtures, &amp;c.

	F.-p. Degs. C.	B.-p. Degs. C.		F.-p. Degs. C.	B.-p. Degs. C.
Wood's metal . . .	60·5	...	Brass . . . . .	880	...
Lichtenberg's metal .	91·6	...	Ferronickel (25% Ni)	1230	...
Rose's metal . . .	93·7	...	Manganese steel (13%		
Newton's metal . . .	94·5	...	Mn) . . . . .	1260	...
Soft solder . . . .	170	...	Blast furnace slag .	1200-1400	...
Bronze . . . . .	790	...			

## 3. Chemical Compounds, Salts.

Picric acid . . . .	122	...	Potassium chloride .	766	...
Ammonium sulphate	140	...	Barium chloride . .	847	...
Mercury bi-chloride .	260	290	Sodium chloride . .	851	...
Caustic soda . . .	310	...	Borax . . . . .	880	...
Silver nitrate . . .	200	...	Potash . . . . .	880	...
Sodium nitrate . . .	316	...	Glauber salt . . . .	900	...
Saltpetre . . . . .	339	...	Potassium sulphate .	1015	...
Potassium chlorate .	359	...	Soda . . . . .	1090	...
Silver chloride . . .	450	...	Alumina . . . . .	2000	...
Potassium iodide . .	625	...	Quicklime . . . . .	2500	...
Potassium bromide .	715	...	Magnesia . . . . .	3000	...
Sodium bromide . . .	727	...	Calcium carbide . .	3000	...
Calcium chloride . .	755	...			

## 4. Resins, Fats, &amp;c.

Ammoniacum . . . .	42-45	...	Amber . . . . .	280	...
Opopanax . . . . .	50	...	Oleic acid . . . . .	14	...
Tolu balsam . . . .	60-65	...	Lard . . . . .	27	...
Benzoin . . . . .	65-80	...	Paraffin . . . . .	45-80	183-300
Guaiacum . . . . .	85	...	Tallow . . . . .	40-51	
Dammar . . . . .	75-100	...	Spermaceti . . . . .	53	...
Gamboge . . . . .	100	...	Palmitic acid . . . .	60	...
Sagapenum . . . . .	100	...	Wax . . . . .	61-90	...
Olibanum . . . . .	110	...	Margarine . . . . .	62	...
Mastic . . . . .	100-183	...	Stearic acid . . . . .	69	...
Elemic . . . . .	120	...	Asphaltum . . . . .	100	...
Caoutchouc (accord-			Grape-sugar . . . . .	146	...
ing to origin) . . .	125-220	...	Sugar . . . . .	160	...
Sandarach . . . . .	150	...			
Camphor . . . . .	175	204			

TABLE VII.—BOILING-POINTS OF VARIOUS LIQUIDS

(See Table VI.)

	B.-p. Degs. C.		B.-p. Degs. C.
Chamber (sulphuric) acid . . . . .	130-338	Paraffin oil . . . . .	260-360
Anthracene . . . . .	360	Petroleum ether . . . . .	36-40-70
Naphthylamine . . . . .	300	Petroleum benzine . . . . .	70-120
Nitrobenzol . . . . .	205-235	Ligroin (petrol) . . . . .	120-135
Nitroglycerin . . . . .	185	Cleaning oil (petrol) . . . . .	135-160
Resorcin . . . . .	276	Lubricating oils . . . . .	300
Retinol . . . . .	235-250	Lubricating oil (valvoline) . . . . .	371
Sulphur chloride . . . . .	138	Glacial acetic acid . . . . .	119
Xylidin . . . . .	212-220	Amyl alcohol (fusel oil) . . . . .	130
Mercury . . . . .	357	Aniline (pure) . . . . .	182
Arsenious chloride . . . . .	134	Dimethylaniline . . . . .	192-194
Glycerin . . . . .	290	Toluidin . . . . .	196-198
Methyl nitrate . . . . .	66	Nitrobenzol . . . . .	207-210
Resin oils . . . . .	200	Xylidin . . . . .	213-218
Ethereal oils . . . . .	above 140	Propyl alcohol (primary) . . . . .	96-97
Oil of turpentine . . . . .	152-160	Propyl alcohol (secondary) . . . . .	80-81
Napthalene . . . . .	216	Normal butyl (primary) . . . . .	115-117
Cresol (cresyl alcohol) . . . . .	200	Iso butyl (secondary) . . . . .	104-105
Carbolic acid (crude) . . . . .	183	Solid butyl (tertiary) . . . . .	80-80½
Thymol . . . . .	230	Isoamyl (primary) . . . . .	127-128
Xylol (dimethylbenzol) . . . . .	136-140	Amyl alcohol (tertiary) . . . . .	99½-100
Photogene (hydrocarbon) . . . . .	100-145-150	Allyl alcohol . . . . .	96-97
Crude solar oil . . . . .	170-200	Camphor oil (light) . . . . .	204
Solar oil . . . . .	250	Camphor oil (heavy) . . . . .	280-300
Petroleum . . . . .	150-166	Carvacrol (from camphor) . . . . .	86-88
		Terpineol (from aniseed oil) . . . . .	216-218

TABLE VIII.—FLASHING-POINTS

	F.-p. Degs. C.		F.-p. Degs. C.
Brandy . . . . .	29	Engine oil, spindle oil . . . . .	135-190
Hollands gin . . . . .	32	Resin oils . . . . .	130
Whisky . . . . .	28	Lard oil . . . . .	240
Sherry, Port wine . . . . .	54	Spermaceti . . . . .	250
Fusel oil . . . . .	46-54	Ether . . . . .	-20
Kaiser oil, Waterwhite . . . . .	40-48	Carbon di-sulphide . . . . .	-20
Petroleum . . . . .	21-23	Petroleum ether . . . . .	-20
Solar oil . . . . .	60	Coal-tar benzol . . . . .	-15
Olive oil . . . . .	215-260	Methyl alcohol (wood spirit). . . . .	0
Rape oil . . . . .	210-305	Toluol . . . . .	7
Cottonseed oil . . . . .	170	Alcohol (95-45 per cent.) . . . . .	14-20
Poppy oil . . . . .	255	Xylol . . . . .	30
Sesame oil . . . . .	255	Oil of turpentine . . . . .	35
Linseed oil . . . . .	316-350	Glacial acetic acid . . . . .	44
Tar . . . . .	48-82	Aniline . . . . .	76
Sludge alkali from petroleum refineries . . . . .	40	Nitrobenzol . . . . .	90
Paraffin . . . . .	158-195	Dimethylaniline . . . . .	76
Kerosene (Russian) . . . . .	27-73	Toluidin . . . . .	85
Lubricating oil . . . . .	260-320	Xylidin . . . . .	97
Lubricating oil for light motors . . . . .	200	Paraffin oils . . . . .	107
		Monochlorbenzol . . . . .	27.5
		Camphor oils . . . . .	55.0

According to Dr. P. N. Raikow, the following alcohols, of the various strengths specified (percentages), give off inflammable vapours at the appended temperatures.

	100%	80%	60%	40%	20%	10%	7½%	5%	4%	3%
Methylalcohol . . . at	9.5°	16.75°	22.75°	30.0°	44.25°	58.75°	65.25°	..	..	..
Ethylalcohol . . . "	12.0	19.0	22.75	26.25	36.75	49.0	..	62.0°	68.0°	..
Propylalcohol (primary) . . "	23.0	29.5	31.25	32.0	33.75	41.0	46.0	52.25	56.0	..
Propylalcohol (secondary) . . "	11.75	17.25	19.25	20.25	28.75	39.25	..	..	..	..
Norm. Butylalcohol (primary) ..	35.0	40.25	41.0	41.5	41.25	..	42.75	..	..	55.0°
Isobutylalcohol . . . "	27.5	33.75	33.75	33.75	34.75	..	36.0	44.25	..	52.25
Butylalcohol (tertiary) . . . "	11.5	15.25	16.25	16.0	..	30.25	..	41.5	..	..
Iso-amylalcohol (primary) . . "	42.0	..	..	..	..	..	..	..	..	..
Amylalcohol (tertiary) . . . "	19.5	26.25	..	..	..	29.25	..	37.5	..	..
Allylalcohol . . . . . "	21.5	27.5	29.25	30.0	33.0	41.75	..	54.5	..	..

Hence the vapours for the most part cease to be inflammable when the percentage strength of the alcohol is as low as 7½ to 3 per cent.

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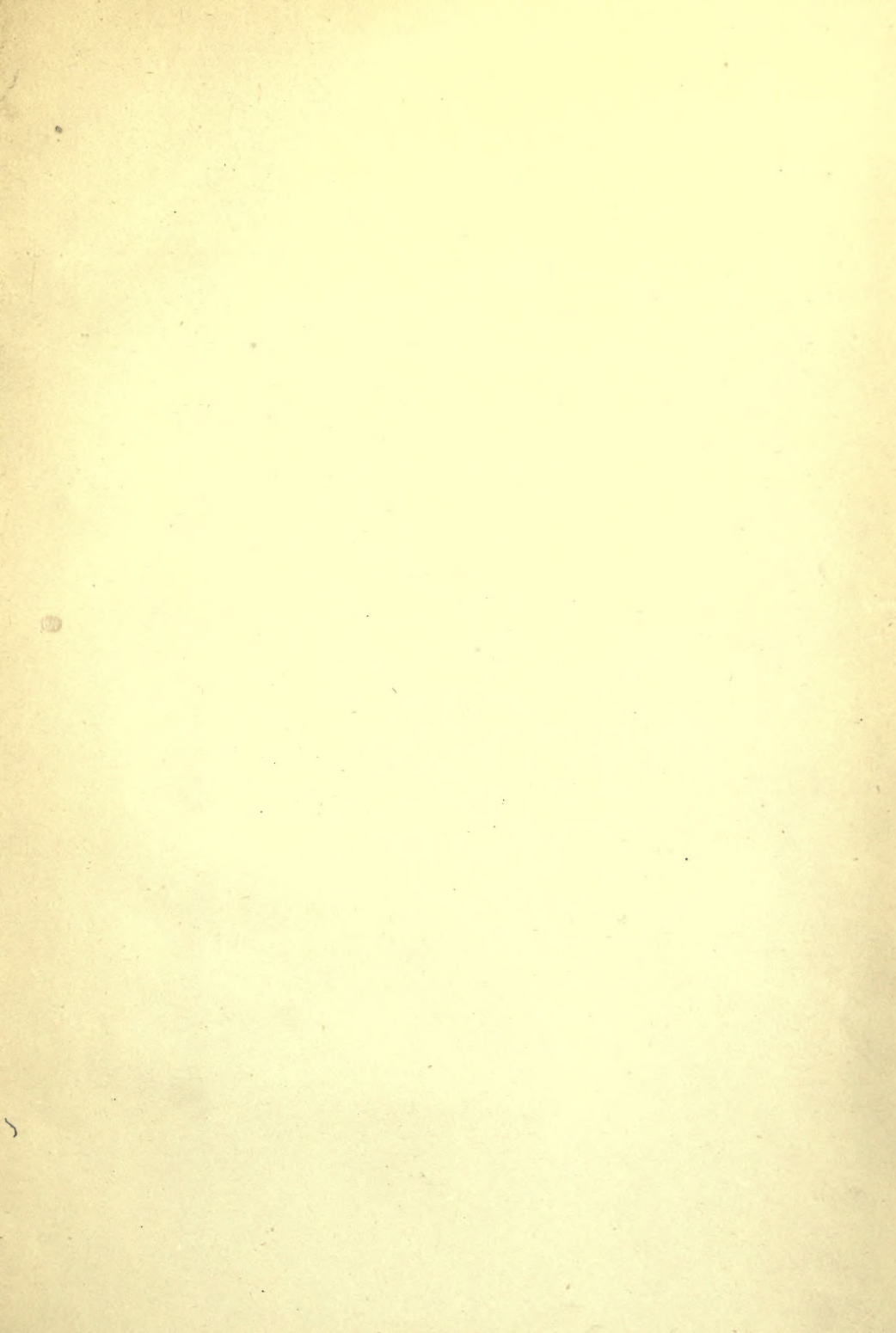
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